



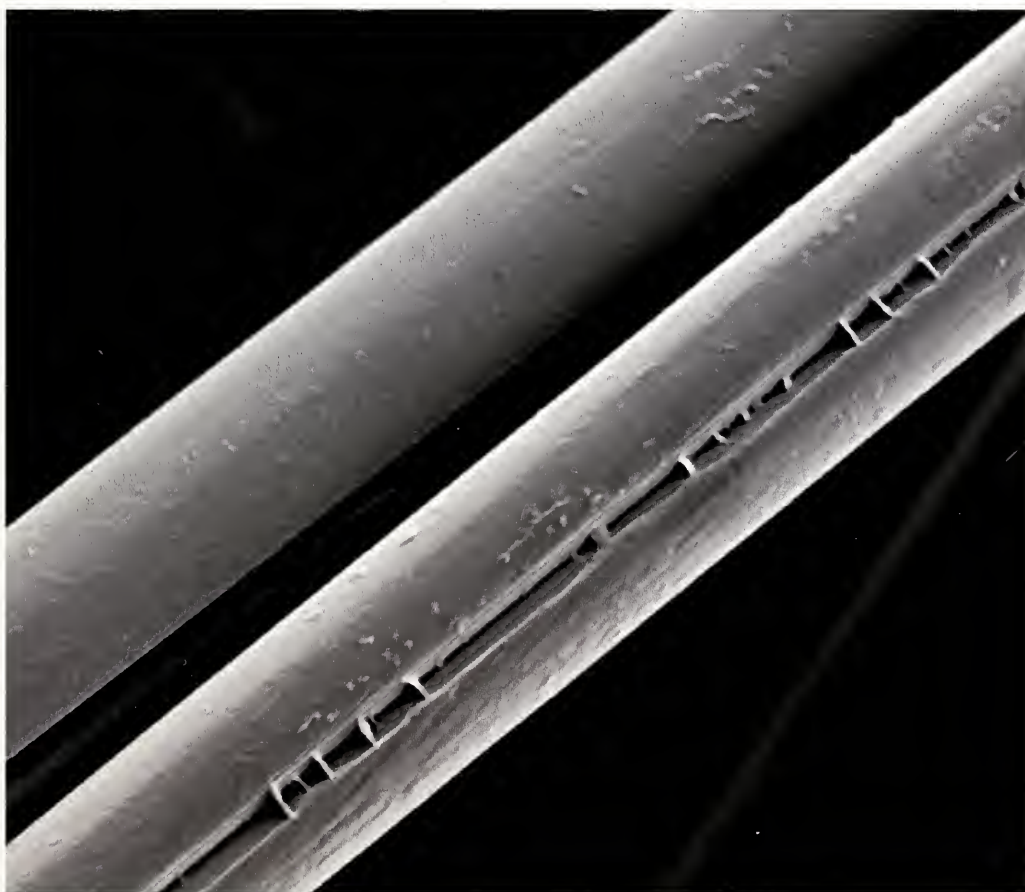
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Chemical and Physical Characterization of Poly(p-phenylene-2,6-benzobisoxazole) Fibers Used in Body Armor

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**Chemical and Physical Characterization of
Poly(p-phenylene-2,6-benzobisoxazole) Fibers
Used in Body Armor**

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ABSTRACT

Problems with the performance and durability of body armor based on poly(p-phenylene-2,6-benzobisoxazole) (PBO) fiber became apparent in the summer of 2003, when PBO-based body armor that had been manufactured less than 8 months earlier was penetrated by a bullet. Mechanical testing of the yarns taken from the penetrated vest indicated a 30 % decrease in tensile strength relative to yarns taken from new, unworn PBO-based vests of the same model. A number of analytical metrologies were used to characterize the yarns, including chemical (elemental and molecular) analysis, mechanical testing, thermal analysis and microscopy. Attenuated total reflectance (ATR) infrared analyses of the yarns revealed differences in their degree of hydrolytic degradation as determined by the presence of benzamide structures. The rank order of reduction in benzamide, which corresponds to benzamide hydrolysis, correlates with the rank order reduction in tensile strengths for these same yarns.

Key Words: body armor, poly(p-phenylene-2,6-benzobisoxazole) (PBO), attenuated total reflectance (ATR), infrared (IR) spectroscopy, fiber, yarn, hydrolysis

INTRODUCTION AND OBJECTIVES

In recent years, high performance fibers based on poly(p-phenylene-2,6-benzobisoxazole) (PBO) have become prominent in high strength applications such as body armor, ropes and cables, and recreational equipment. Problems with the performance and durability of PBO-based body armor became apparent to the law enforcement community in the summer of 2003, when ballistic penetration of PBO-based body armor occurred in three separate incidents.

The first incident involved the shooting of a police officer near Pittsburgh, PA (hereinafter referred to as the “officer”) in June 2003. The bullet pierced the officer’s PBO-based body armor, which had been manufactured less than 8 months earlier. Mechanical testing of the yarns taken from the officer’s vest indicated a 30 % decrease in tensile strength relative to yarns taken from new, unworn PBO-based vests of the same model. Subsequently, two other incidents involving the penetration of PBO-based body armor by a bullet occurred that same year, but the evidentiary circumstances surrounding these incidents are more complicated and not as well documented and, as such, will not be discussed here.

These events prompted the Department of Justice (DOJ) and U.S. Attorney General John Ashcroft to announce a Body Armor Safety Initiative on November 18, 2003 [1], which tasked the National Institute of Justice (NIJ), the research, development and evaluation arm of DOJ, to address technical issues associated with PBO-based body armor. In response to the Attorney General’s initiative, NIST’s Office of Law Enforcement Standards (OLES) and research groups within the NIST laboratories have undertaken a parallel, multi-phase effort to characterize chemical and physical degradation of PBO fiber and to correlate this degradation to body armor durability.

The primary goals of the work described in this report, which comprises Phase I of the research program, were to:

- Identify metrologies for characterizing the chemical, physico-mechanical and morphological properties of PBO fibers extracted from the officer's vest, new, unworn vests, and virgin PBO yarn.
- Utilize the above-identified analytical metrologies to carry out a comprehensive study of the chemical, physico-mechanical and morphological properties of the abovementioned yarns.
- Identify fiber properties that are correlated with the tensile properties of PBO.

The research detailed in this interim report is ongoing and will be updated as new findings become available. Future phases of this research program will address degradation mechanisms, accelerated aging and prediction of PBO fiber service life.

OVERVIEW OF PBO

Poly(p-phenylene-2,6-benzobisoxazole), or PBO, is a member of the benzazole polymer family and is characterized by the heterocyclic benzobisoxazole group in its main chain structure, as shown in Figure 1. The conjugated benzobisoxazole and phenyl rings in the PBO repeat unit contribute to extended π -electron delocalization and molecular rigidity, which provides high thermal stability and outstanding mechanical properties to this class of polymers. The chemistry and processing of PBO and related polymers has been documented [2, 3] and is not discussed here.

PBO fibers, as are the majority of the polybenzazole-based fibers, are extremely strong, tough and stiff, with tensile strengths and moduli superior to those of polyaramid or ultra-high molecular weight polyethylenes. Like carbon and other organic fibers, the axial compressive strength of PBO is quite low, being approximately 10 % to 15 % of the

tensile strength. One explanation for this low compressive strength is that the intermolecular/interfibrillar forces in PBO are weak, allowing slippage of polymer chains or fibrils to occur under compressive load. Compressive failure is often accompanied by the formation of kink bands, which has been explained by some researchers to be the result of fibrillar instability [4].

The morphology and structure of PBO has been studied extensively using X-ray scattering, X-ray diffraction and various microscopic techniques, including scanning electron microscopy, transmission electron microscopy, and atomic force microscopy. It is generally accepted that PBO fiber has a fibrillar structure made up of extended, oriented PBO molecules, with individual fibril diameters ranging from 7 nm into the micron range [5]. Kitagawa et al. studied PBO using small angle X-ray scattering (SAXS) and transmission electron microscopy and observed that capillary voids nominally 2 nm to 3 nm in diameter and 30 nm long exist between the microfibrils in the fiber core. It was later determined that these capillary voids contain water that had been trapped in the fiber during the spinning process [6]. It has also been observed that the skin region of PBO fiber exhibits a higher degree of molecular orientation than the core region [7] and is essentially void-free [5].

A number of questions exist concerning the hydrolytic and ultraviolet (UV)-visible light stability of PBO. The manufacturer has reported tensile strength degradation of PBO fiber following exposure to heat and moisture [8]. Only a few studies in the peer-reviewed literature provide any data on the hydrolytic stability of PBO in aqueous and acidic conditions. As far back as 1995, researchers at NASA evaluated the chemical resistance of PBO and observed significant losses in tensile strength following immersion

in water, hydrochloric acid, nitric acid, sulfuric acid, sodium chloride and sodium hypochlorite [9]. More recently, So et al. studied PBO fiber as well as model compounds of PBO in a variety of acidic and basic conditions [10]. Bond cleavage in PBO fiber was observed when it was dissolved in hot methane-sulfonic acid; no changes in relative molecular mass were observed following exposure to sulfuric acid, poly(phosphoric acid) or sodium hydroxide.

An extensive review conducted of the organic chemistry literature on hydrolysis of simple oxazoles and benzoxazole compounds can be found in Appendix A. This review summarizes findings that indicate, in general, that oxazoles and benzoxazoles undergo hydrolysis in conditions ranging from neutral to acidic, and at ambient as well as elevated temperatures.

A number of low relative molecular mass benzoxazole-containing compounds have been documented to undergo ring-opening upon exposure to ultraviolet and/or visible radiation [11, 12, 13]. Only one study could be found that documents the effects of ultraviolet-visible radiation on PBO fibers, in which substantial (> 90 %) loss in tensile strength was observed following 450 h exposure to 340 nm radiation [9].

EXPERIMENTAL PROCEDURES*

Vest Materials

The comparative analysis of PBO materials included yarns from:

- The back panel of the officer's vest, manufactured in November 2002. This material will be referred to as the "officer's" vest. The front panel, where the bullet penetration occurred, is currently being retained as evidence and could not be obtained for analysis at the time of this writing.
- A new, unworn vest of the same model and construction as the officer's vest, style SMU-IIA+105130, manufactured in September 2003. This material will be referred to as the "new" vest.
- A vest from the National Law Enforcement and Corrections Technology Center (NLECTC) Compliance Test Program Archive, style SMU-IIA+105130, manufactured in March 2001; and submitted for compliance testing in May 2001. This material will be referred to as the "archive" vest.
- PBO spool yarn, manufactured in August 2003 and provided to NIST by the fiber manufacturer in May 2004 for this study. This material will be referred to as "virgin" yarn.

The ballistic panels from the vests described above consist of 20 layers of woven PBO fabric stacked together and diagonally stitched. For use in the field, the ballistic panel is typically inserted into a moisture-permeable plastic liner, referred to as the covering. The panel and covering are then inserted into a cotton fabric carrier.

Yarn Extraction Procedure

Forty horizontally oriented (weft) yarns were extracted from the tenth layer of each vest. In the officer's vest, the eleventh layer was used because the tenth layer was

* Certain commercial equipment, instruments or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for this purpose.

diagonally oriented. Nitrile gloves were worn throughout the extraction procedure to minimize contamination due to handling. Seams were first carefully removed from the ballistic panel to free the layers. Yarns were then extracted one by one from the bottom of the 10th layer using with a small hook, and wrapped in aluminum foil that had been cleaned with methanol and acetone. This yarn removal process is depicted in Figure 2. Each foil packet was labeled with vest name, layer number and yarn number. Virgin yarn was used directly off of the spool.

Tensile Testing

To obtain yarn mechanical properties, tensile testing of yarns was carried out in accordance with ASTM D2256-02, “Standard Test Method for Tensile Properties of Yarn by the Single-Strand Method”, using an Instron Model 4482 test frame equipped with a 91 kg (200 lb) load cell, and pneumatic yarn and cord grips (Instron model 2714-006). Jaw separation was 7.9 cm (3.1 in) and cross-head speed was 2.3 cm/min (0.9 in/min). In this study, yarns were nominally 38.1 cm (15 in) long, and given 60 twists on a custom-designed yarn twisting device. This level of twist was maintained on the yarns as they were inserted into the pneumatic yarn and chord grips. Six replicates from each vest were tested to failure. The standard uncertainty of these measurements is typically $\pm 5\%$.

Microscopy

Laser Scanning Confocal Microscopy—A Zeiss Model LSM510 reflection laser scanning confocal microscope (LSCM) was employed to characterize the surface morphology. The incident laser wavelength was 543 nm. By moving the focal plane in

the z-direction, a series of single images (optical slices) can be stacked and digitally summed over the z-direction to obtain a 3-D image. The z-direction step size was 0.5 μm using objectives of 5x and 10x, and 0.1 μm using objectives of 20x, 50x, and 150x.

Scanning Electron Microscopy—Scanning electron microscopy (SEM) analysis was carried out on a FEI Quanta 600 scanning electron microscope using secondary electron imaging at accelerating voltages ranging from 2 kV to 15 kV. Fibers were mounted on aluminum stubs using carbon tape and were sputter coated with gold to conduct excess charge and enhance the secondary electron emission.

Atomic Force Microscopy—To observe the surface morphology of the fibers on the nanoscale, atomic force microscopy (AFM) was carried out on a Dimension 3100 scanning probe microscope (Veeco Metrology) in tapping mode. Commercial silicon microcantilever probes (TESP, Veeco Metrology) were used. Topographic and phase images were obtained simultaneously using a resonance frequency of approximately 300 kHz for the probe oscillation and a free-oscillation amplitude of $62\text{ nm} \pm 2\text{ nm}$.

Thermogravimetric Analysis (TGA)

TGA was carried out on a TA Instruments 2950 high resolution thermogravimetric analyzer. Yarn samples of approximately 30 mg were coiled to fit into 500 μL alumina sample pans. Samples were equilibrated at 27 $^{\circ}\text{C}$ for 5 min, and then ramped to 1000 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C}/\text{min}$. Analyses were carried out in both air and nitrogen atmospheres, with 5 replicates measured in air and 2 replicates of each sample measured in nitrogen. The primary parameters of interest were the temperature at which 5 % mass loss was reached in the samples, as well as the % mass loss at 110 $^{\circ}\text{C}$. The relative

standard uncertainty in the mass loss measurements is typically $\pm 0.1 \%$, and the standard uncertainty in the temperature scale is typically $\pm 0.1 ^\circ\text{C}$.

X-ray Photoelectron Spectroscopy (XPS)

XPS measurements were performed on a Kratos Axis Ultra photoelectron spectrometer. Experiments were conducted at room temperature and an average base pressure of 1.3×10^{-6} Pa. The monochromatic Al K_α X-ray source was operated at 140 W (14 kV, 10 mA). The energy scale was calibrated with reference to the Cu $2p_{3/2}$ and Ag $3d_{5/2}$ peaks at binding energies (BEs) of 932.7 eV and 368.3 eV, respectively. A coaxial charge neutralization system provided charge compensation. Yarns were attached to the XPS sample holder using Cu tape. The analysis area for the high-resolution spectra was 2 mm x 1 mm. The Na 1s, O 1s, N 1s, K $2p_{3/2}$, C 1s, P 2p, and Si 2p spectra were acquired at a take-off angle of 45° and a pass energy (PE) of 20 eV, and a maximum acquisition time of 8 min per element.

Peak BEs were determined by referencing to the adventitious C 1s photoelectron peak at 285.0 eV. Quantitative XPS analysis was performed with the Kratos VISION software (version 2.1.2). Atomic concentrations were calculated from the photoelectron peak areas by subtracting a linear-type background. The P 2p region was deconvoluted using mixed 70 % Gaussian/30 % Lorentzian components. Uncertainty in the peak BE measurement is typically ± 0.2 eV and atomic concentration uncertainties are typically ± 1 atomic %.

X-ray Fluorescence (XRF) Spectroscopy

XRF analysis was carried out on a PANalytical model PW2404 wavelength dispersive XRF. Two 26 mm diameter fabric swatches from each vest were analyzed. Measurements were made in vacuum (≈ 15 Pa) using a Rh X-ray source operating at an average power of 3.0 kW. Elements having higher energy characteristic X rays were measured using generator settings of 60 kV and 50 mA. Elements having lower energy characteristic X rays were measured using generator settings of 30 kV and 100 mA. Elemental composition calculations were carried out using the IQ+ fundamental parameters method, contained in the SuperQ operating system software of the XRF instrument. Calibration of the instrument and IQ+ method was carried out using reference materials, including NIST Standard Reference Materials (SRMs), which enabled the total relative standard uncertainty in elemental composition measurements to be estimated at 10 %.

X-ray Diffraction (XRD)

X-ray powder diffraction patterns were obtained with a Bruker D8 Advance diffractometer using Cu K_{α} radiation ($\lambda = 1.5405$ nm) with a step size of 0.02° and a step time of 3 s. Specimens were analyzed as fabric swatches or as multiple yarn strands (nominally 3 cm long) tautly stretched and attached to a XRD sample holder with adhesive tape. Beam direction was parallel to the longitudinal axis of the fiber. Standard uncertainty in peak intensities is estimated to be ± 2 %.

Fourier Transform Infrared (FTIR) Spectroscopy

Infrared analysis was carried out using a Nicolet Nexus FTIR equipped with a mercury-cadmium-telluride (MCT) detector and a SensIR Durascope attenuated total reflectance (ATR) accessory. Consistent pressure on the yarns was applied using the force monitor on the Durascope. Dry air was used as the purge gas. FTIR spectra were recorded between 4000 cm^{-1} and 700 cm^{-1} at three different locations on each yarn and were averaged over 128 scans. Spectral analysis, including spectral subtraction, was carried out using a custom software program developed in the Polymeric Materials Group at NIST to catalogue and analyze multiple spectra [14]. All spectra were baseline corrected and normalized using the aromatic C-H deformation peak at 848 cm^{-1} . Standard uncertainties associated with this measurement are $\pm 2\text{ cm}^{-1}$ in wavenumber and $\pm 1\%$ in absorbance.

RESULTS AND DISCUSSION

Tensile Testing

Tensile properties of yarns extracted from the back panel of the officer's vest, a new vest, and an archive vest are detailed in Table 1. The yarns from the officer's vest are clearly lower in ultimate tensile strength and ultimate tensile strain than the yarns from the new and archive vests, as well as the virgin yarn. The tensile strengths of the yarns from the archive vest are also lower than that of the new vest and virgin yarns. Interestingly, the moduli of the yarns from the three vests are not substantially different.

The difference between the tensile properties of the virgin yarn and the vest yarns may be due to the degradation in strength that results from handling and weaving of the yarn into fabric.

Microscopy

In Figures 3-7, confocal microscopy and SEM images of fibers from vest and virgin yarns show morphological features that are tentatively identified as pits, transverse cracks and longitudinal grooves. Based on qualitative confocal microscopy analysis of 20 to 25 fibers from each vest, no prominent differences are observed in the surface morphology of the fibers from the three different vests.

Using optical and transmission and electron microscopy, similar transverse cracks observed by Chau et al. 1995 [15] have been postulated to be kink bands. Kink bands have also been observed in the microscopic analysis of other rigid rod polymers such as polyaramid and polybenzothiazole (PBT) [16,17]. As discussed earlier, kink bands result from compressive loading or bending encountered during processing, handling, or end-use. Kink bands are also known to initiate the formation of voids or cracks, which may subsequently degrade fiber tensile properties [18].

The longitudinal grooves are believed to have originated in the fiber spinning operation, but their exact cause is unknown. A 3-D image topographic profile generated by compiling confocal image slices of one such longitudinal groove is displayed in Figure 4. Groove depth and width were estimated by topographic measurements to be $(0.70 \text{ to } 0.84) \mu\text{m} \pm 0.05 \mu\text{m}$, and $(0.75 \text{ to } 0.95) \mu\text{m} \pm 0.05 \mu\text{m}$, respectively.

Both AFM topographic and phase images of PBO fiber surfaces exhibit an oriented fibrillar morphology that has been observed by other researchers [19, 20, 21]. An AFM image of the officer's vest fibers are shown in Figure 8; similar results were obtained for the fibers from the other vests as well as from the virgin fiber. Patchy regions on the surface are attributed to sizing compounds that were applied after the fiber spinning operation. Similar features have also been observed by Tamargo-Martinez et al. [19]. In some instances, as shown in Figure 8, AFM analysis reveals disordering of the oriented fibrils, which may be associated with kink band formation. However, it is not certain that these disordered regions correspond to the cracks or kink bands observed via confocal microscopy and SEM, because it is difficult to find the exact location of a feature observed on two different size scales using two different imaging tools.

Thermogravimetric Analysis (TGA)

In thermogravimetry, the mass loss of a specimen is monitored as a function of time at a fixed temperature or as a function of temperature at a fixed heating rate. In polymers, thermal mass loss curves can provide information on the material's thermal stability, the composition of multicomponent materials, and/or the presence of low molecular mass or volatile components. Data from TGA analysis of PBO yarns are detailed in Table 2.

In a nitrogen atmosphere, the decomposition temperature at 5 % mass loss of the yarns from the officer's vest is lower relative to the other two vest yarns and the virgin yarn; however, this small difference in light of the standard uncertainty is not statistically significant. Mass loss at 110 °C, attributed to the loss of water and/or low relative

molecular mass materials, is similar for the vest and virgin yarns. In air, little difference in the mass loss at 110 °C or the 5 % decomposition temperature are observed. These thermogravimetry results are consistent with Kuroki et al. [22].

X-ray Photoelectron Spectroscopy (XPS)

In XPS, specimens are irradiated with X rays, causing electrons to be ejected from the core atomic levels of atoms contained in the specimen. From the kinetic energies of the ejected electrons - termed photoelectrons - electron binding energies can be calculated which uniquely define a specific atom. Chemical shifts in binding energies can be correlated to changes in the chemical environment of an atom, and can be used to identify oxidation state and/or the nature of other atoms bound to that atom [23]. Because the mean-free paths of the ejected photoelectrons are extremely short, XPS is a surface-sensitive technique, providing information on the topmost 4 nm of a specimen surface.

XPS atomic concentrations of elements found on the yarn surfaces are presented in Table 3. The surface elemental compositions of the yarns from the different vests are nominally identical. In addition to the expected carbon, oxygen and nitrogen, silicon, phosphorus, potassium, silicon and sodium are also observed. Phosphorus is postulated to originate from residual poly(phosphoric acid) spinning solvent and/or the fiber sizing that is applied by the fiber manufacturer. Silicon is also attributed to the fiber sizing. Sodium is believed to originate from the sodium hydroxide solution used to neutralize excess poly(phosphoric acid). Tamargo-Martinez et al. [19] also observed similar atomic concentrations in their XPS analysis of virgin PBO yarns.

It is worth noting that the theoretical atomic concentrations of 77.8 atomic % carbon, 11.1 atomic % oxygen and 11.1 atomic % nitrogen calculated from the PBO polymer repeat unit do not match the measured atomic concentrations of these elements listed in Table 3. Reasons for this discrepancy are the presence of sizing agents (as mentioned above), the presence of adventitious surface organic compounds, and/or the preferential surface enrichment of particular segments of the polymer chain.

The ratio of phosphorus and sodium is of interest because sodium hydroxide is used in the PBO manufacturing process to neutralize the poly(phosphoric acid) spinning solvent, which is contained in and on the fiber immediately after spinning. Complete neutralization of poly(phosphoric acid) by sodium hydroxide would result in the formation of a sodium phosphate compound, in which the atomic ratio of phosphorus to sodium should range between 0.3 to 1.0, depending on the specific type of sodium phosphate compound formed. The atomic ratio of phosphorus to sodium in the vest yarns ranges from 1.75 to 2.6, indicating that phosphorus is present in quantities beyond that which can be accounted for by sodium phosphate.

Photopeak energies were analyzed to determine the identity of the sodium and phosphorus compounds detected. The binding energy of the phosphorus 2p photopeak in the vest yarns falls in the range from 133.2 eV to 133.4 eV (referenced to carbon at 285.0 eV) and that of the sodium 1s photopeak falls between 1071.5 eV and 1071.7 eV. These photopeak energies are consistent with Na_3PO_4 , which is documented to have phosphorus 2p binding energies between 132.5 eV to 133.1 eV, and sodium 1s binding energies between 1071.2 eV and 1071.5 eV [24]. If poly(phosphoric acid) was present, the binding energy of the phosphorus 2p photoelectrons would be in the neighborhood of

135.4 eV, which is higher than the phosphorus detected in the vest yarns. Therefore, it is concluded that no detectable poly(phosphoric acid) residues are present on the fiber surface; rather, the phosphorus that is present is consistent with that of sodium phosphate or some other phosphate compound, possibly the fiber sizing.

X-ray Fluorescence (XRF) Spectrometry

In XRF analysis, as in XPS, a specimen is irradiated with a beam of sufficiently short wavelength X rays, resulting in the generation of fluorescent X rays having energies characteristic of the elements present in the specimen. Quantitative information on the elements in the specimen can be obtained by measuring the count rates of the emitted X rays. XRF is a rapid, sensitive, and accurate method for detecting inorganic materials and metals in polymers, with minimal sample preparation needed (as compared to wet chemical elemental analysis methods) [25]. Unlike XPS, which is a surface analysis technique, XRF obtains elemental information from deeper in the fiber bulk.

Table 4 shows the elemental compositions of the vest yarns as measured by XRF. The two elements of particular interest, phosphorus and sodium, are found to be the most abundant and in essentially identical mass concentrations in each of the 3 vest materials. Phosphorus mass fractions range from 0.45 % to 0.48 %. Using an inductively-coupled plasma (ICP) elemental analysis technique, a phosphorus content of 0.4 % was found in virgin PBO yarn by Hu and Lesser [26], which is consistent with the present study.

As discussed previously in the section on XPS, neutralization of phosphoric acid by sodium hydroxide results in the formation of some type of sodium phosphate compound, in which the mass ratio of phosphorus to sodium could range from 0.45 to

1.35, depending on the specific type of sodium phosphate compound formed. The phosphorus/sodium mass ratio in the vest yarns ranged from 1.45 to 1.59, indicating that phosphorus is present in quantities beyond that which can be accounted for by sodium phosphate.

Figure 9 overlays phosphorus K-M series X-ray lines from each yarn specimen. The ratio of net count rates for these two peaks is 3.8. Data from other compounds of phosphorus and oxygen show that the net peak ratios are 3.1 for phosphorus pentoxide (P_2O_5), 3.9 for lithium phosphate (LiPO_3), and 5.0 for phosphoric acid (H_3PO_4). Thus, a peak ratio of 3.8 most closely corresponds to PO_3 , or phosphate, moiety. These results complement the XPS analyses, which also suggest that a phosphate-type compound accounts for the phosphorus that is detected.

It should be noted that the presence of a phosphate-containing sizing compound on the fiber surface could potentially absorb the fluorescent X rays generated by atoms inside the fibers and would complicate the analysis of the phosphorus K-M series X-ray lines. Thus, the presence of the sizing makes it difficult to determine the exact nature of any phosphorus-containing species inside the fiber. To make a definitive identification of phosphorus compounds, including phosphoric acid, ^{13}P nuclear magnetic resonance (NMR) may be a more useful technique.

X-ray Diffraction

The scattering of X rays by atoms in a crystal lattice results in a diffraction pattern that is characteristic of the crystal structure. In highly crystalline polymers such as PBO,

an X-ray diffraction pattern can reveal the degree of crystallinity, crystal orientation, and provide input for the calculation of crystal lattice parameters [27].

According to detailed crystal structure analysis performed by Tashiro et al., the proposed structure for PBO is a monoclinic cell with $a = 11.2 \text{ \AA}$, $b = 3.57 \text{ \AA}$, $C = 12.01 \text{ \AA}$, and $\gamma = 100.6^\circ$, corresponding to 2 polymer repeat units per cell [28]. The PBO chain in the crystal structure has been observed to have an almost perfectly planar conformation. Davies et al. have reported differences in crystallite orientation between the skin and the core regions of PBO fiber analyzed with X-ray diffraction [29].

The equatorial X-ray diffractograms shown in Figure 10 reflect the intermolecular arrangement between packed polymer chains in the PBO fibers. Diffractograms obtained in our lab are consistent with those reported by other researchers [29, 30, 31, 32]. Major crystalline peaks are observed at $2\theta = 16.2^\circ$, 27.5° , and 32.7° , corresponding to crystal lattice d-spacings of 0.547 nm, 0.324 nm and 0.274 nm, respectively.

No significant differences in the locations of the crystalline peaks or any changes in the peak structures are observed for yarns or fabric swatches from the three vests. Differences in peak intensity are most likely due to differences in the packing density of the fiber samples. Substantial changes in the crystal lattice structure would be accompanied by changes in peak shape and location, as seen by Tamargo-Martinez et al., who reported significant changes in the equatorial X-ray diffractogram of PBO fiber as it is heated up to 800°C [30].

Infrared Spectroscopy

The interaction between materials and the infrared region of the electromagnetic spectrum provides valuable information on the molecular structure of organic materials, including organic polymers. Specific functional groups absorb at given frequencies corresponding to their vibrational modes. Changes in the intensities or frequencies of observed spectral peaks can be correlated to changes in the molecular structure of the compound. This type of information is valuable for mechanistic and kinetic studies of polymer degradation.

Figures 11(a) and 11(b) show the ATR infrared spectra of the vest yarns compared with the spectrum of virgin yarn. The primary infrared bands are listed in Table 5. Assignments are made on the basis of literature data [30,33, 34, 35, 36] and studies carried out in our lab using model compounds. Benzoxazole and 2-phenyl benzoxazole model compounds were analyzed to identify the peaks in the PBO spectrum that are attributed to the oxazole or benzoxazole component in the PBO structure. Two small peaks, shown on an expanded scale in Figure 11(c), are observed at 1726 cm^{-1} and 1691 cm^{-1} in all yarns analyzed. These peaks have not been reported in any previous publications or observed in our analysis of benzoxazole-containing model compounds.

Visual examination of the yarn spectra does not highlight any obvious chemical differences between the yarns. In many instances, chemical changes due to polymer degradation are often difficult to detect directly. Spectral subtraction, in which a reference spectrum is subtracted from the spectrum of a material of interest, is often helpful in extracting small chemical changes and providing information on the formation and depletion of specific functional groups.

Figure 12 shows the difference spectra that result when the infrared spectrum of the virgin yarn is subtracted from each of the vest yarn spectra. Qualitatively similar difference spectra are obtained when the spectrum of the yarns from the new vest were subtracted from the officer and archive vest yarn spectra. Downward-pointing, or negative, peaks in the difference spectra are species that are lower in concentration relative to the reference spectrum (virgin yarn, in this case) and upward-pointing, or positive, peaks are species that are higher in concentration relative to the reference material or new species that are not originally present in the reference material.

The primary negative peaks in the difference spectra of the vest yarns are seen at 931 cm^{-1} , 1072 cm^{-1} , 1422 cm^{-1} , 1440 cm^{-1} , 1506 cm^{-1} , 1560 cm^{-1} , 1588 cm^{-1} , 1657 cm^{-1} and 3400 cm^{-1} . These peaks are not found in the unsubtracted infrared spectra of the vest yarns or the virgin yarn. However, subsequent infrared analysis of a known benzoxazole hydrolysis product, N-(2-phenylhydroxybenzamide), revealed peaks at 931 cm^{-1} , 1070 cm^{-1} , 1441 cm^{-1} , 1657 cm^{-1} and 3400 cm^{-1} that matched a number of the negative peaks in the difference spectrum.

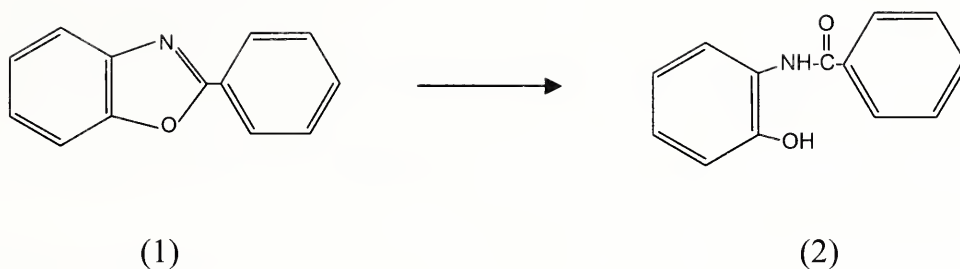
The following degradation scenario is proposed on the basis of the ATR-infrared data available at this time: it is postulated that benzamide-type structures similar to N-(2-phenylhydroxybenzamide) exist in the vest yarns as well as the virgin yarn. These species are found in low concentrations and are not visible in the original unsubtracted infrared spectra. These species are possibly the result of benzoxazole ring hydrolysis that occurred during processing/storage/handling, UV-visible light exposure (as documented for benzoxazole-containing model compounds in [37] and [38]), or some combination of these. As the yarns are woven, fabricated into body armor, and worn in

the field, additional hydrolysis of the benzamide structures could occur. Benzamide hydrolysis would result in the formation of aminophenol and benzoic acid species, and a consequent reduction in the concentration of the original benzamide structures. This decrease in benzamide concentration is the origin of the negative peaks that appear when the virgin yarn infrared spectrum is subtracted from the infrared spectra of the vest yarns.

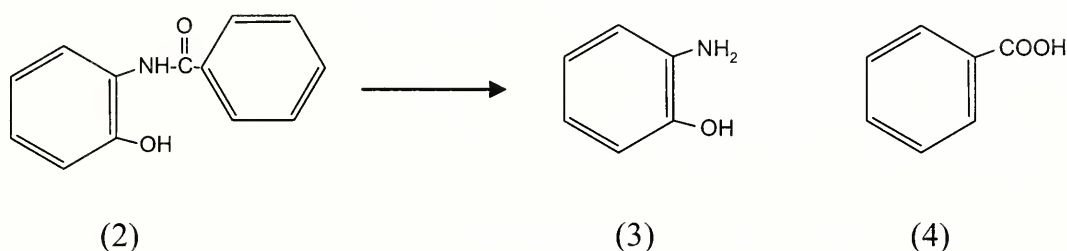
The difference spectrum of the officer's vest yarn contains negative benzamide peaks with the highest intensity (absorbance), followed by the archive vest and the new vest, in decreasing order of intensity. This indicates that the degree of benzamide hydrolysis is greatest in the officer's vest, followed by the archive vest, and the least in the new vest, relative to the virgin yarn. This rank order in benzamide peak absorbance follows the same rank order of tensile strength loss reported earlier. Figure 13 shows a plot of vest yarn tensile strength plotted against the absorbance of negative peaks corresponding to benzamide species. A negative correlation is observed to exist between tensile strength and benzamide peak spectral absorbance.

A number of positive peaks in the difference spectra correspond to peaks that are present in the original spectrum of virgin PBO. This could indicate that a higher concentration of benzoxazole structures is present in the vest yarns relative to the virgin yarn. The remaining positive peaks in the difference spectra are not identified at the present time; infrared analysis of known benzoxazole degradation products, such as benzoic acid and aminophenol will be carried out to assign these peaks.

Support for the hydrolysis of benzoxazole to benzamide and the regeneration of benzoxazole from benzamide is given by Jackson et al. [39]. When 2-phenylbenzoxazole (1) is heated in an acidic medium, N-(2-phenylhydroxybenzamide) (2) is first formed:



N-(2-phenylhydroxybenzamide) can then further hydrolyze to 2-aminophenol and benzoic acid ((3) and (4), respectively), or re-convert to 2-phenylbenzoxazole (1).



Both benzoxazole hydrolysis and benzamide hydrolysis mechanisms potentially cause tensile strength degradation in PBO – the first by disrupting the conjugated rigid rod structure and creating a polyaramid-type structure in its place; the second by chain scission. In the present study, the latter mechanism appears to be predominant. In theoretical models of fiber tensile strength and modulus developed by Termonia et al.[40] and Jones and Martin [41], both groups state that decreases in polymer chain length are more detrimental to tensile strength than to elastic modulus. These observations are consistent with the vest yarn tensile properties reported in this study, in which degradation was observed in tensile strength but not elastic modulus.

SUMMARY

A number of analytical metrologies were used in characterizing the chemical, physico-mechanical and morphological properties of PBO yarns from an officer's vest penetrated by a bullet, a new vest, a vest from the NLECTC Compliance Test Program archive, and virgin PBO yarn. Metrologies used to characterize the yarns included chemical (elemental and molecular) analysis, mechanical testing, thermal analysis and microscopy. Results of these analyses were used to determine if any chemical or morphological differences exist between the four different yarns and if any of these properties were correlated to yarn tensile properties.

Very few differences were observed in the surface or bulk elemental composition of the yarns; phosphate compounds that were detected on all yarns were attributed to either fiber sizing materials or acid neutralization products. Additionally, no detectable differences were observed in the crystal structure of the fibers nor in their surface morphologies. Transverse and longitudinal cracks were observed, however, on all of the analyzed fibers.

ATR infrared analyses of the yarns revealed differences in their degree of hydrolytic degradation as determined by the presence of benzamide structures. Benzamide structures were observed to different degrees in the officer's vest yarn, new vest yarn, archive vest yarn and virgin PBO yarn. The rank order of reduction (hydrolysis) in benzamide species correlates with the rank order reduction in tensile strengths for these same yarns. This ordering is significant since benzamide hydrolysis is believed to contribute to tensile strength loss via chain scission.

ACKNOWLEDGMENTS

The authors thank NIST's Office of Law Enforcement Standards (OLEs) and the National Institute of Justice (NIJ) for their support of this research, as well as the Tekne Group for assistance in tensile testing.

Table 1: Tensile Properties of Vest Yarns

	Ultimate Tensile Strength (GPa)	Strain at Break (%)	Modulus at Break (GPa)	Energy to Break Point (N m)
<u>Officer</u>				
Mean*	3.22	2.50	136.61	0.31
Std Dev	0.24	0.17	2.61	0.04
Minimum	2.90	2.32	134.00	0.26
Maximum	3.48	2.68	140.48	0.35
<u>New</u>				
Mean*	4.78	3.29	141.80	0.61
Std Dev	0.19	0.12	3.61	0.05
Minimum	4.47	3.18	137.98	0.53
Maximum	5.02	3.42	146.24	0.66
<u>Archive</u>				
Mean*	3.65	2.65	141.60	0.37
Std Dev	0.10	0.06	5.00	0.02
Minimum	3.53	2.55	134.89	0.35
Maximum	3.78	2.74	148.32	0.39
<u>Virgin</u>				
Mean*	5.34	3.52	147.11	0.91
Std Dev	0.16	0.12	2.70	0.05
Minimum	4.85	3.19	142.85	0.75
Maximum	5.53	3.67	152.84	0.99

* n (number of replicates) = 6

Table 2: Thermogravimetric Analysis of Vest Yarns

Sample ID	Percent Mass Loss at 110 °C	5 % Decomposition Temperature (°C)
<u>Nitrogen Atmosphere</u>		
Officer	0.10 ± 0.04	692.1 ± 1.5
New	0.13 ± 0.06	694.4 ± 1.5
Archive	0.17 ± 0.10	694.0 ± 2.8
Virgin	0.26 ± 0.09	699.4 ± 8.2
<u>Air Atmosphere</u>		
Officer	0.33 ± 0.10	632.8 ± 2.1
New	0.32 ± 0.09	632.0 ± 3.4
Archive	0.28 ± 0.08	632.9 ± 4.8
Virgin	0.48 ± 0.17	633.6 ± 2.5

Table 3: Elemental Analysis by X-ray Photoelectron Spectroscopy (XPS) of Vest Yarns

SAMPLE	C 1s BE (eV)	AC (%)	O 1s BE (eV)	AC (%)	N 1s BE (eV)	AC (%)	P 2p BE (eV)	AC (%)	K 2p BE (eV)	AC (%)	Si 2p BE (eV)	AC (%)	Na 1s BE (eV)	AC (%)
Officer 1	285.0	76.4	532.6	14.2	398.8	3.1	133.4	1.5	292.9	1.3	102.2	2.7	1071.7	0.7
Officer 2	285.0	77.3	532.5	13.6	399.0	3.4	133.4	1.4	292.9	1.3	102.1	2.2	1071.7	0.8
New 1	285.0	76.5	532.5	14.4	398.7	3.0	133.5	1.8	292.8	1.4	102.1	2.2	1071.7	0.7
New 2	285.0	76.6	532.5	14.0	398.7	2.9	133.2	2.2	292.8	1.4	102.0	2.0	1071.7	1.0
Archive 1	285.0	77.5	532.8	13.4	398.7	3.7	133.6	1.6	292.7	1.1	101.9	1.8	1071.5	0.8
Archive 2	285.0	76.7	532.3	14.4	398.7	3.1	133.6	1.7	292.8	1.4	102.1	2.0	1071.6	0.8

Table 4: Elemental Analysis by X-ray Fluorescence Spectroscopy of Vest Yarns
(All values in mass fraction %)

	Officer 1	Officer 2	New 1	New 2	Archive 1	Archive 2
Mass (g)	0.17	0.20	0.21	0.20	0.22	0.26
Area (cm²)	16.0	17.2	18.2	19.8	16.0	25.2
Na	0.29	0.30	0.33	0.32	0.29	0.29
Al	*	*	0.002	*	0.003	0.006
Si	0.030	0.027	0.024	0.029	0.021	0.023
P	0.45	0.46	0.48	0.47	0.46	0.47
S	*	*	*	*	0.003	0.002
Cl	0.010	0.010	0.009	0.011	0.010	0.008
K	0.051	0.050	0.053	0.048	0.045	0.045
Ca	0.018	0.019	0.022	0.028	0.014	0.013
Ti	0.005	*	0.004	0.004	0.002	0.003
Fe	0.009	0.008	0.007	0.008	0.002	0.003
Cu	0.003	0.003	0.003	0.003	*	0.001
Sr	0.023	0.008	0.023	0.022	0.003	0.006

* Not detected above 0.001 %

Table 5: FTIR-ATR Band Assignments for PBO Fiber

<u>Band</u> (cm ⁻¹)	<u>Assignment</u>
3097	Aromatic C-H stretch from benzene between oxazole rings, closer to oxygen
3069	Aromatic C-H stretch from benzene between oxazole rings
3040	Aromatic C-H stretch from phenyl ring
2956	Aliphatic C-H stretch (sizing)
2910	Aliphatic C-H stretch (sizing)
2851	Aliphatic C-H stretch (sizing)
1726	
1691	
1619	C=C stretching in substituted aromatic rings, cyclic C=N stretching
1577	Skeletal vibrations in conjugated system/benzoxazole ring
1557	Skeletal vibrations in conjugated system/benzoxazole ring
1496	Skeletal vibrations in conjugated system/benzoxazole ring
1461	Skeletal vibrations in conjugated system/benzoxazole ring
1412	
1367	
1329	C-N stretching
1308	C-N stretching
1276	C-C stretching in carbons linking oxazole and aromatic ring; O-C=N stretching
1210	
1147	Asymmetric stretching of unsaturated cyclic ether
1114	Aromatic C-H in-plane bending
1056	Asymmetric stretching of unsaturated cyclic ether
1010	Aromatic C-H in-plane bending
925	Symmetric C-O-C stretching of cyclic ether
914	Symmetric C-O-C stretching of cyclic ether
869	Aromatic C-H out of plane bending
848	Aromatic C-H out of plane bending
821	Aromatic C-H out of plane bending
701	Aromatic C-H out of plane bending

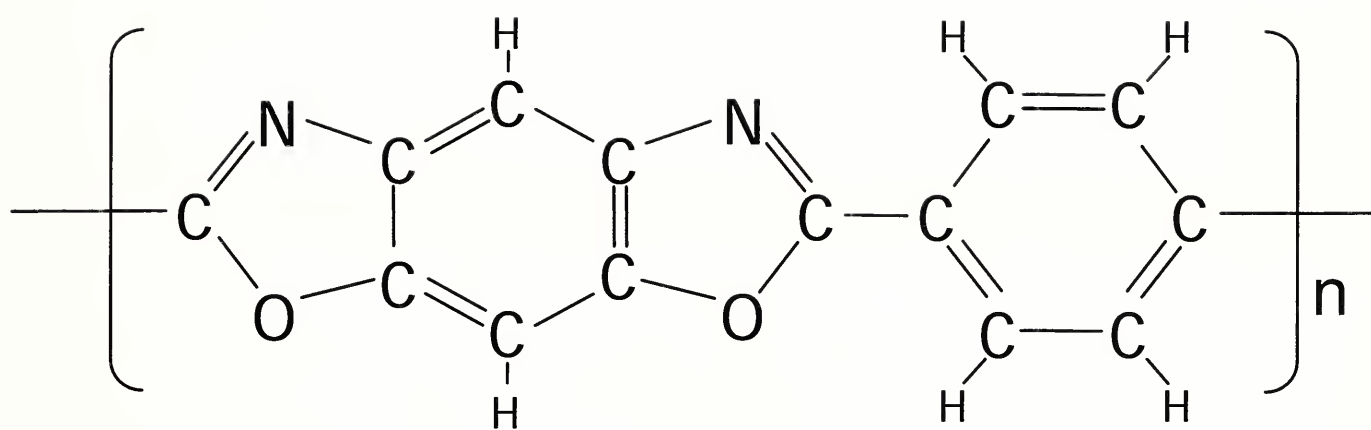
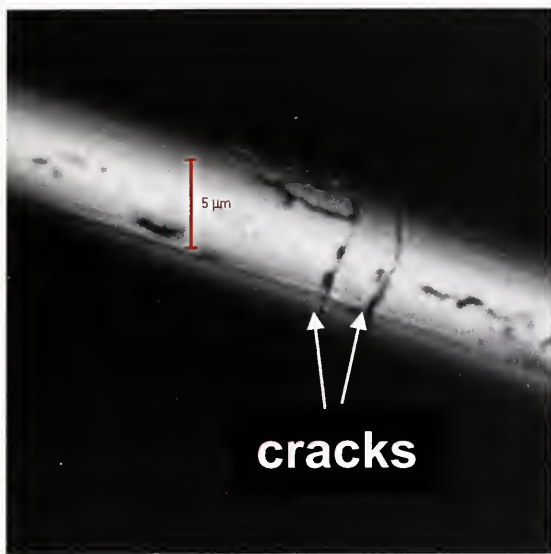


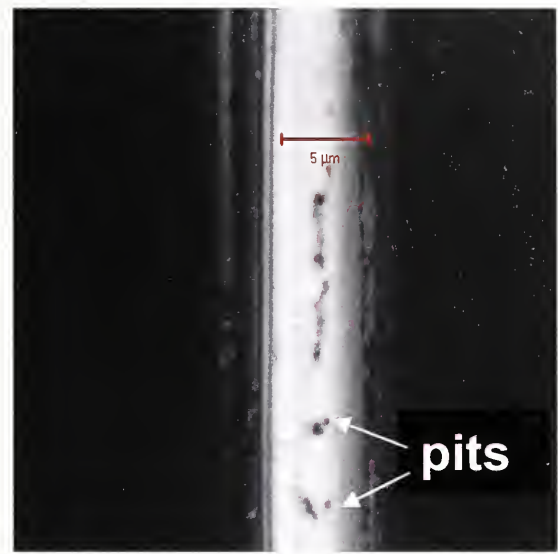
Figure 1: Chemical structure of poly(p-phenylene-2,6-benzobisoxazole), or PBO



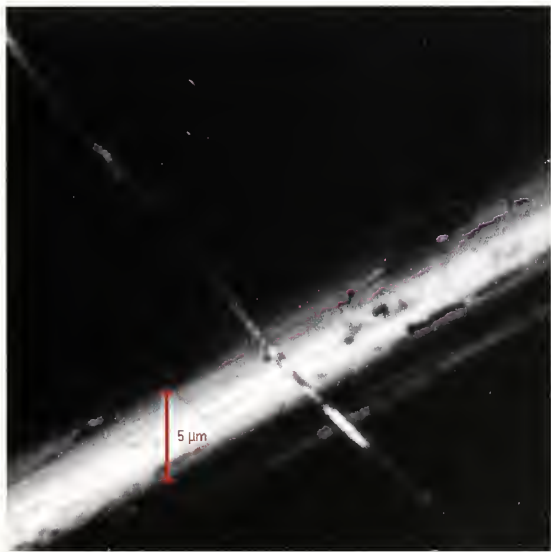
Figure 2: Extraction of yarns from ballistic panels in vests.



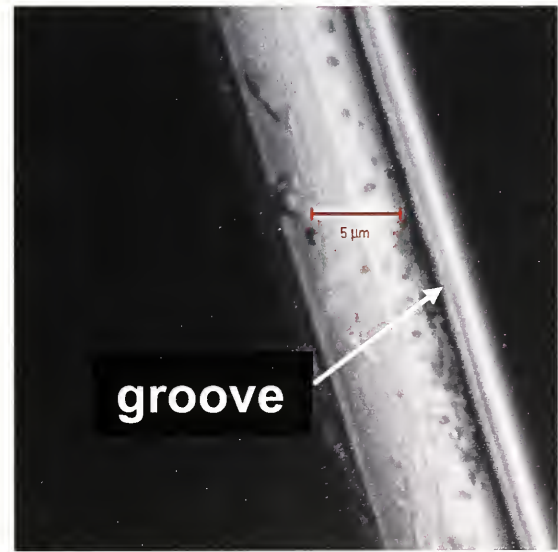
(a)



(b)



(c)



(d)

Figure 3: Confocal microscope images of fibers from (a) officer's vest, (b) new vest, (c) archive vest, and (d) virgin PBO fiber.

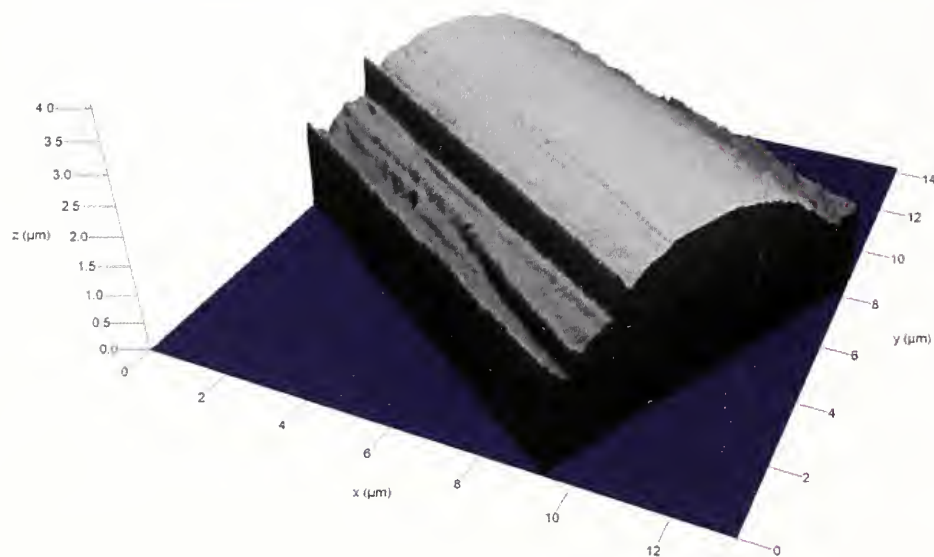
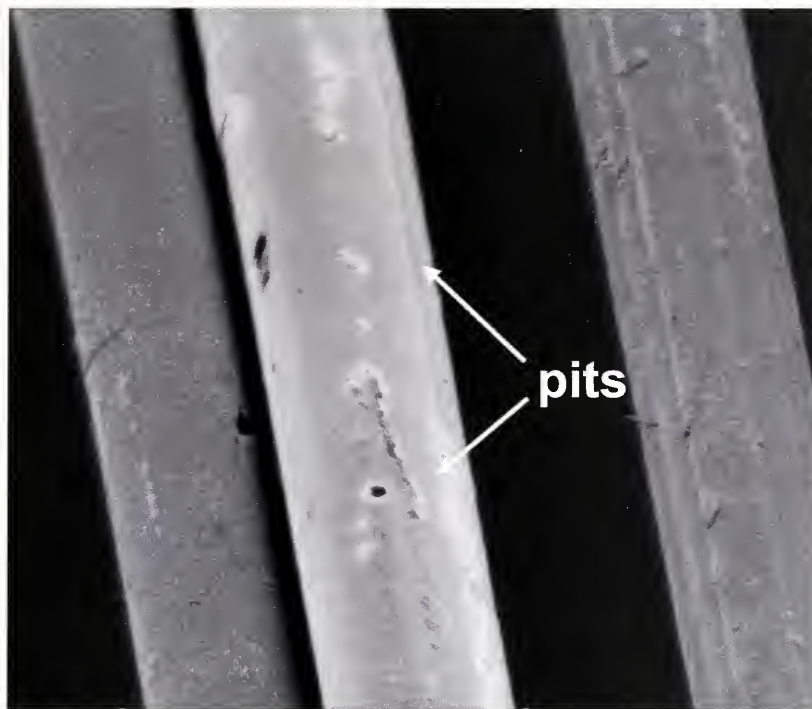
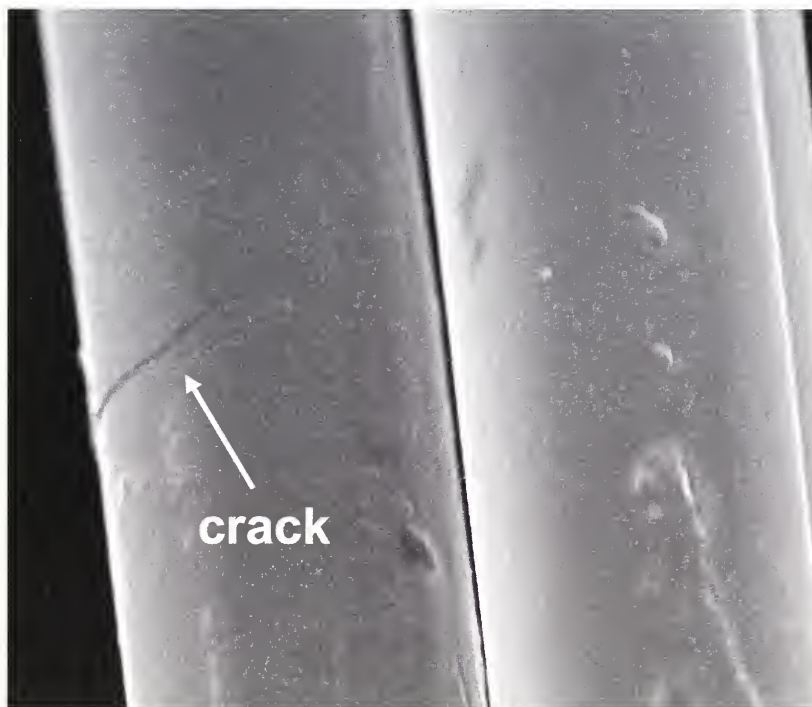


Figure 4: 3-D profile of the longitudinal groove seen in the confocal microscope image of virgin fiber, above.

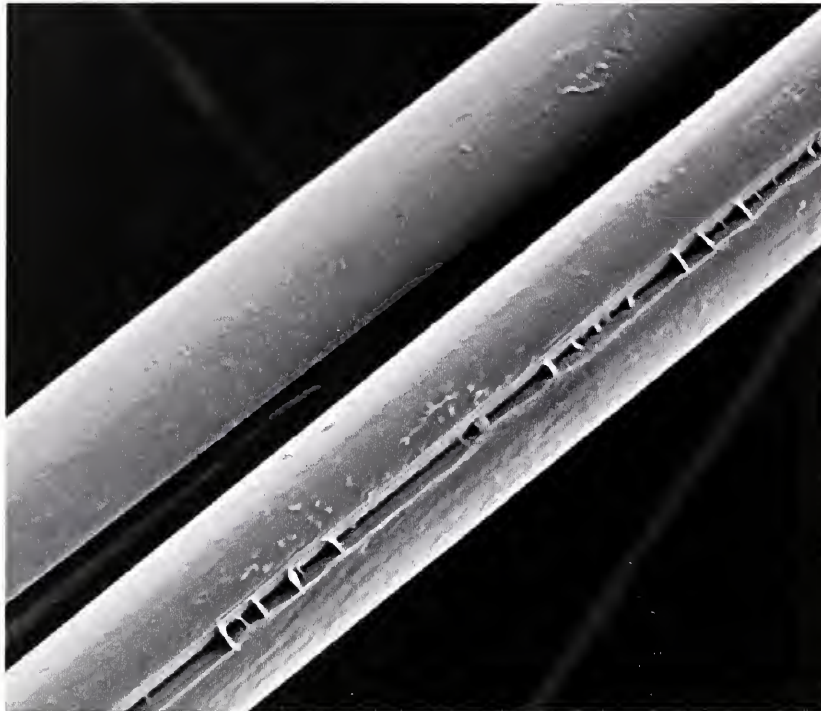


500 V, 5 kx, 50 μ m field width
(a)

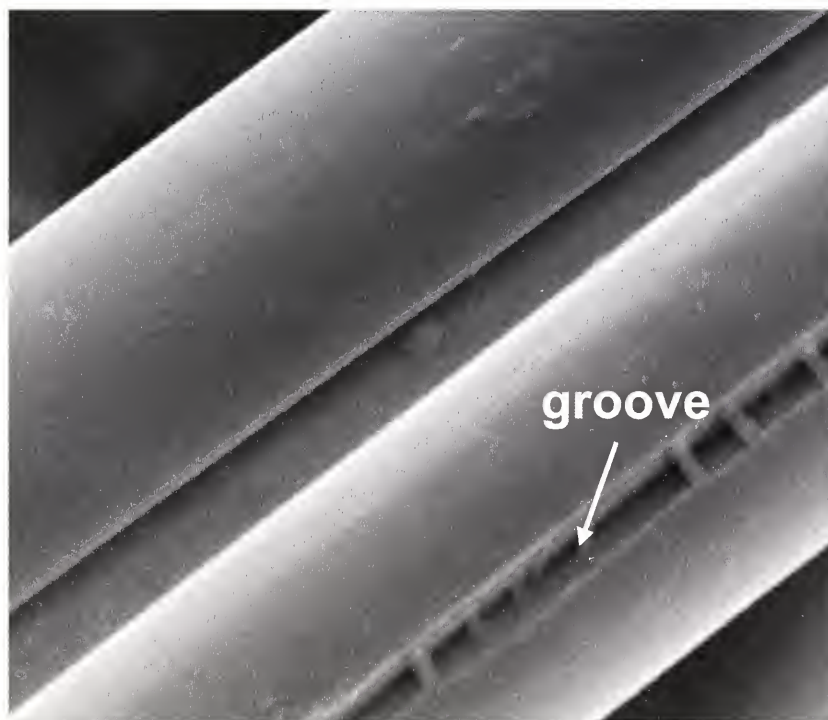


25 kV, 10kx, 25 μ m field width
(b)

Figure 5: SEM micrographs of fibers from officer's vest.

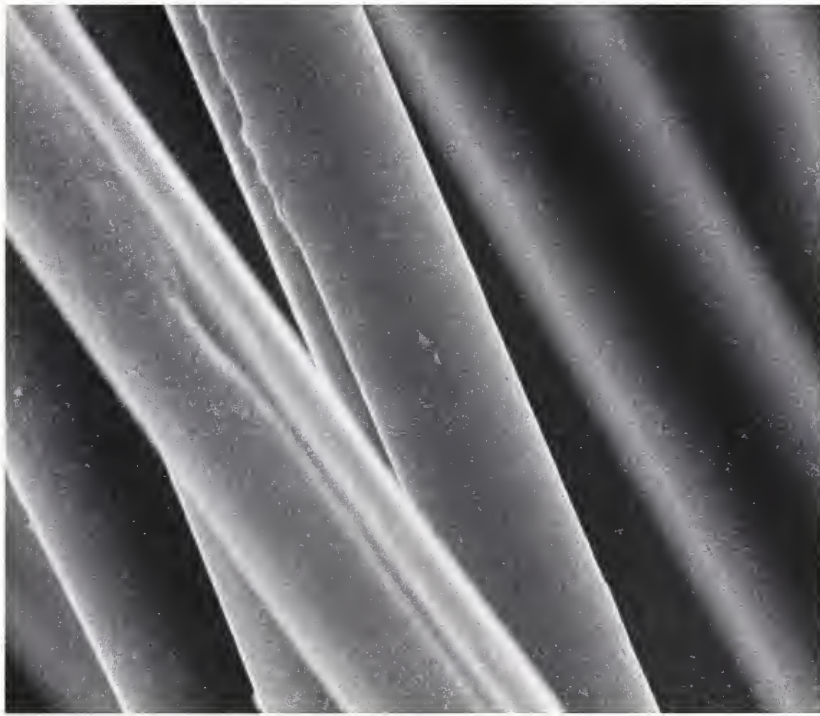


25 kV, 5 kx, 50 μm field width
(a)



25 kV, 10 kx, 25 μm field width
(b)

Figure 6: SEM micrographs of fibers from new vest.

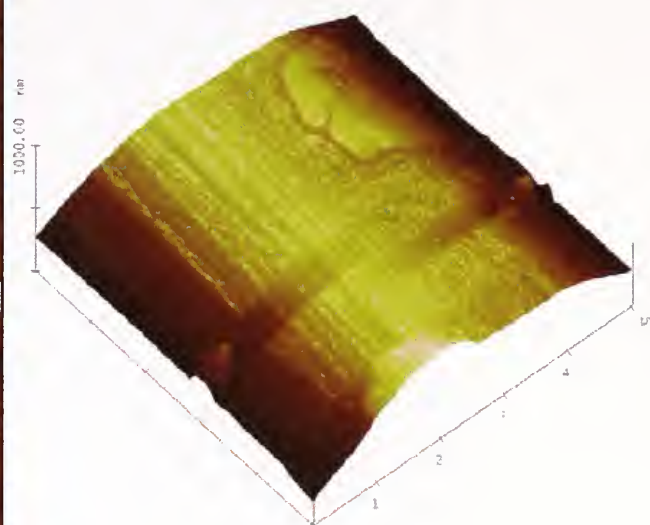


25 kV, 5 kx, 50 μ m field width

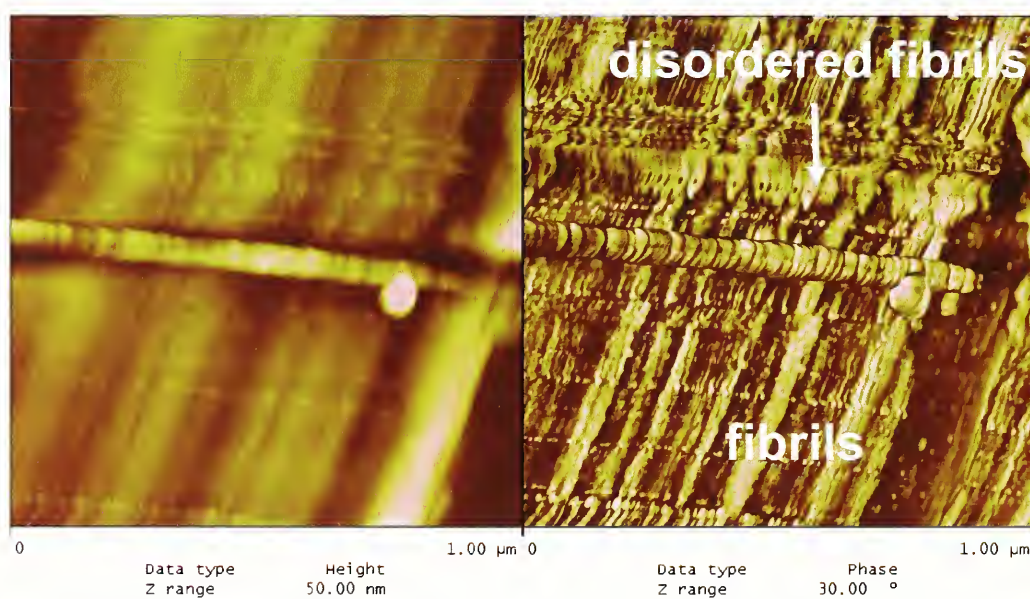
Figure 7: SEM micrographs of fibers from archive vest.



(a)



(b)



(c)

Figure 8: AFM micrographs of PBO fiber. (a) Phase image of fiber from officer's vest; (b) 3-D depiction of region shown in (a); (c) topographic and phase images of disordered region in fiber from officer's vest.

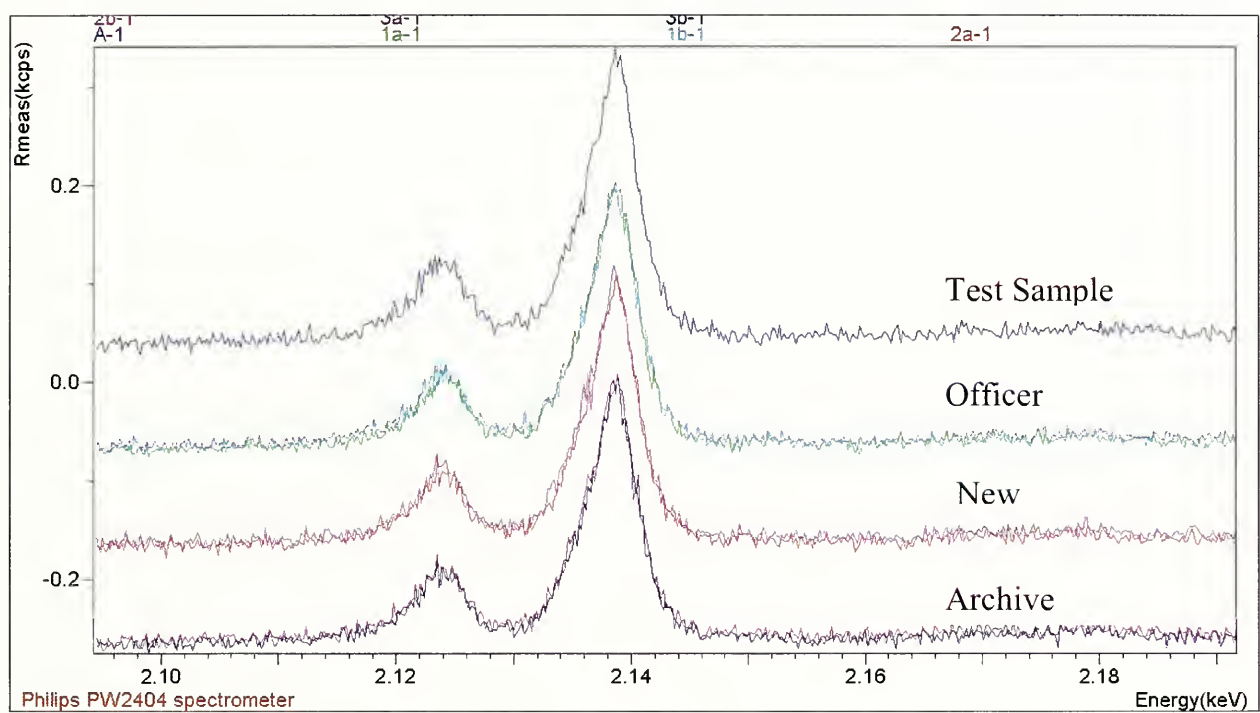


Figure 9: Phosphorus K-M series lines from vest yarns. Two scans from each vest are superimposed.

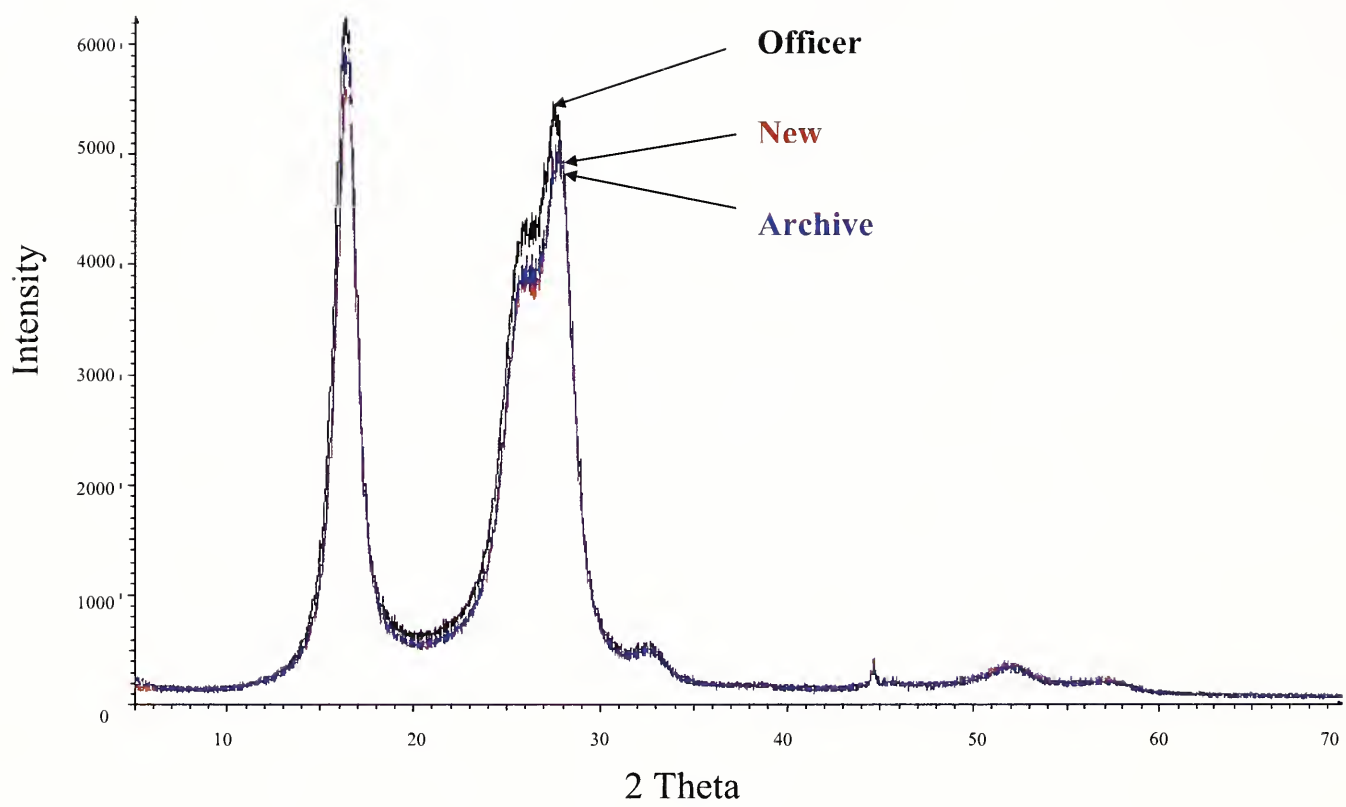
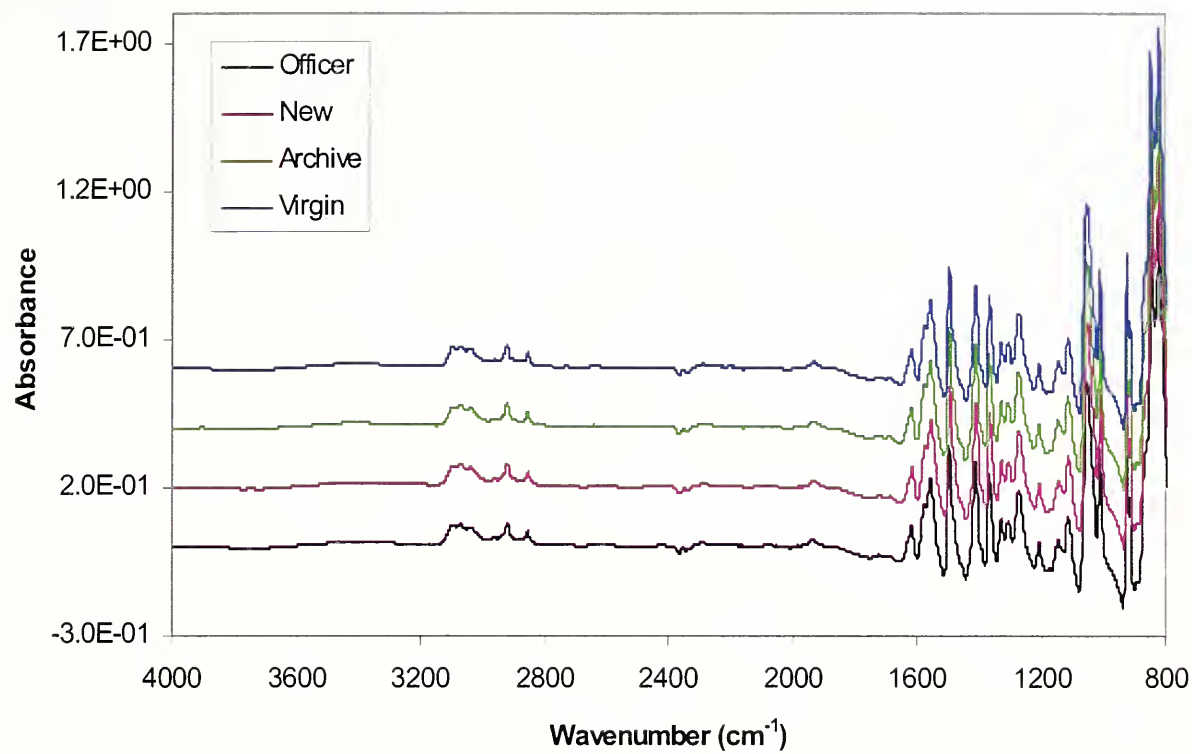
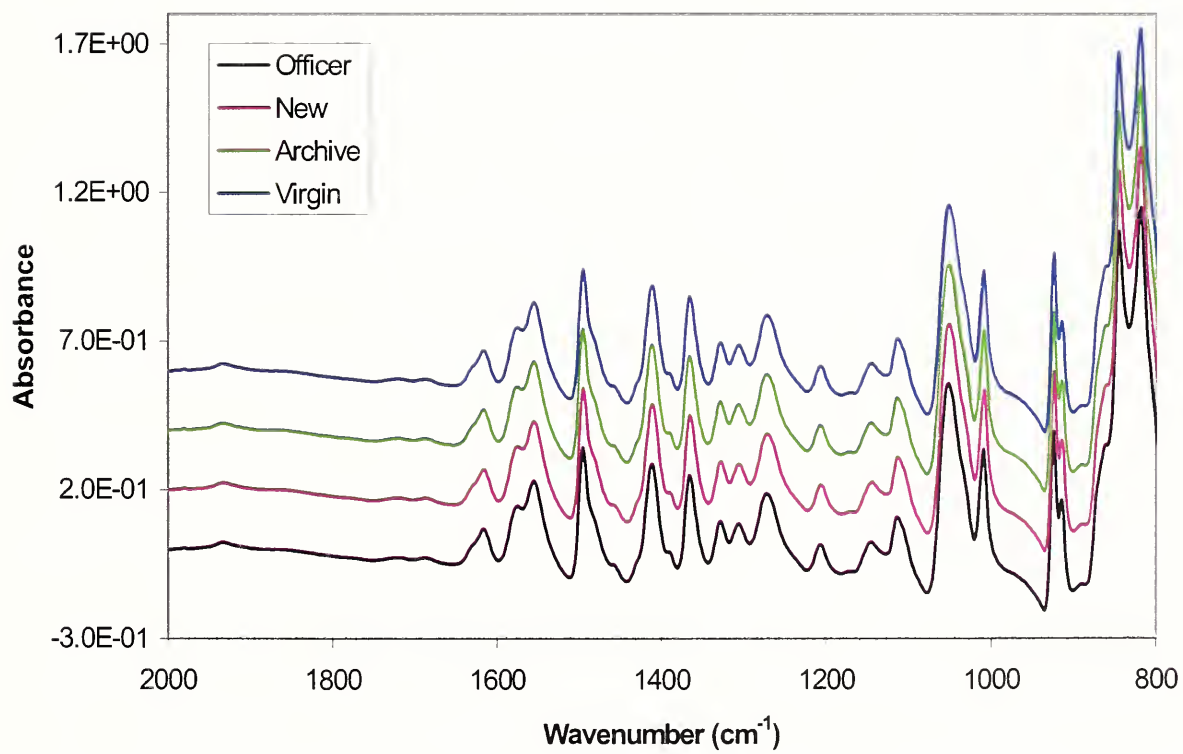


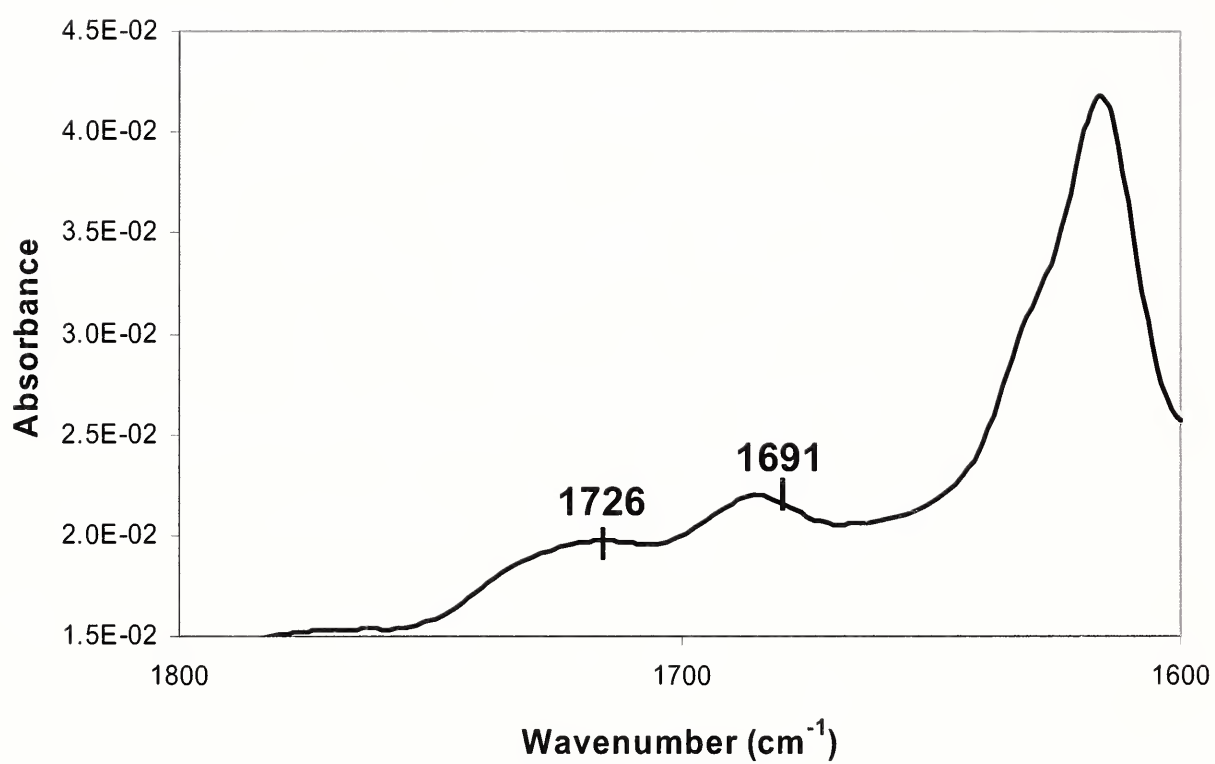
Figure 10: Comparison of equatorial x-ray diffractograms from vest yarns.



(a)

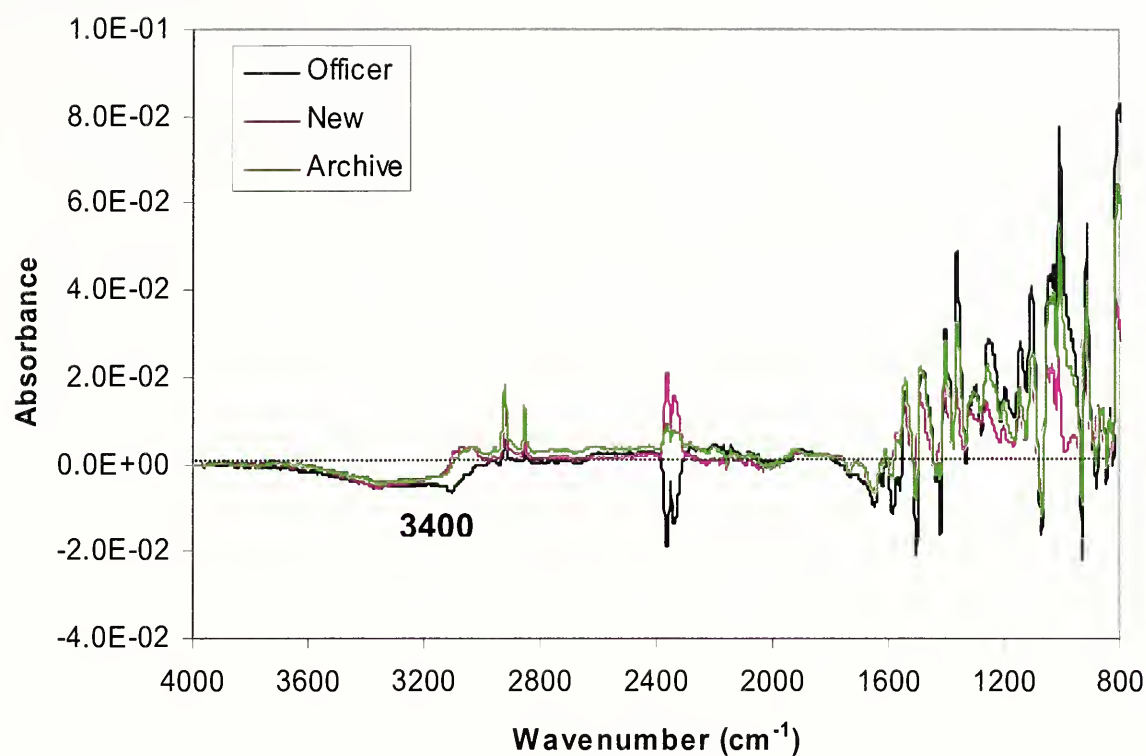


(b)

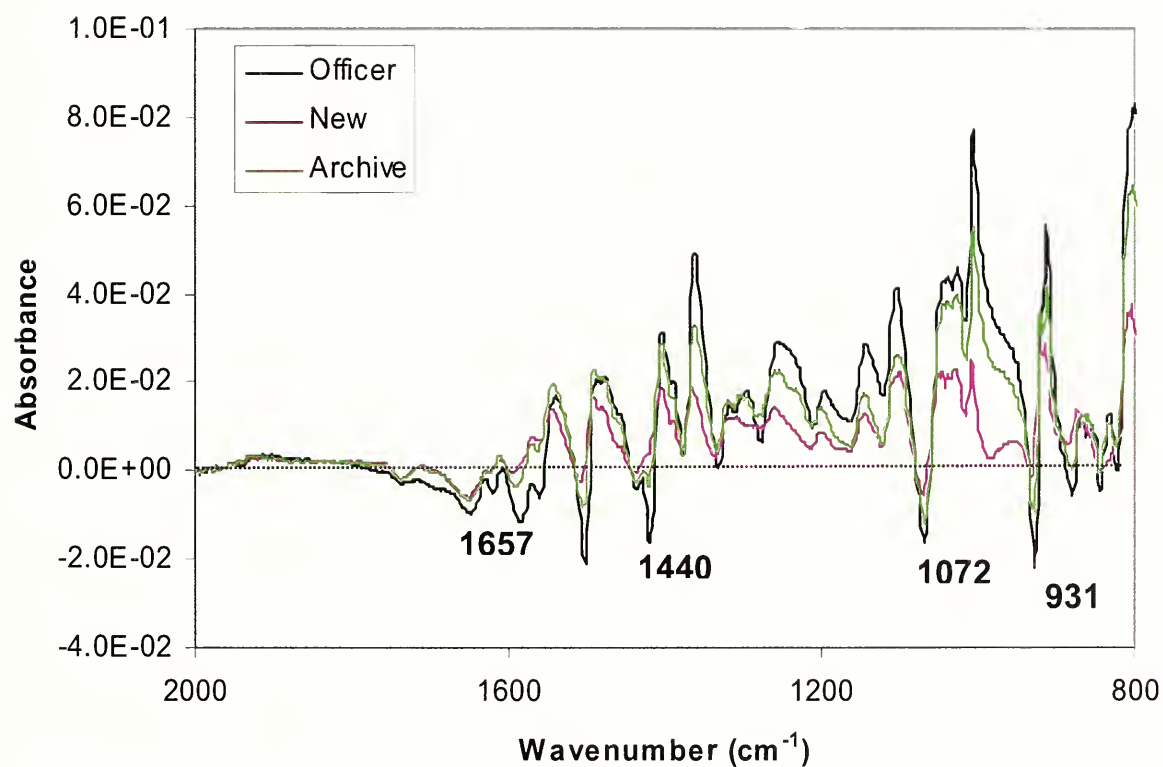


(c)

Figure 11: (a), (b) FTIR spectra of vest yarns, compared with virgin yarn. (c) Peaks at 1691 cm⁻¹ and 1726 cm⁻¹, observed in the infrared spectrum of all yarns analyzed.



(a)



(b)

Figure 12: Difference spectra of vest yarns (referenced to spectrum of virgin yarn). Peaks matching those observed in the spectrum of N-(2-phenylhydroxybenzamide) are labeled.

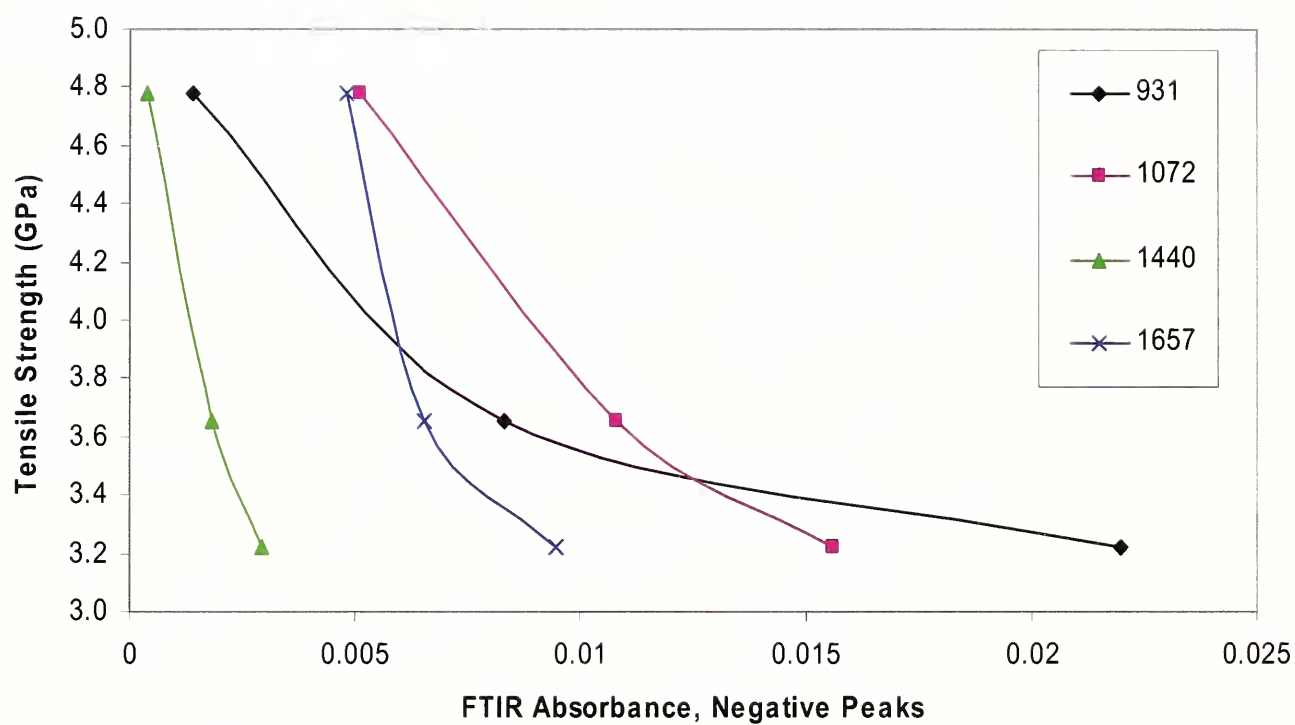


Figure 13: Vest yarn tensile strength plotted against the absorbance of negative subtraction peaks corresponding to benzamide species.

REFERENCES

1. Department of Justice Bulletproof Vest Safety Initiative, 03-624
<http://www.ojp.gov/pressreleases/DOJ03624.htm>.
2. J.F. Wolfe, "Polybenzothiazoles and Oxazoles", in *Encyclopedia of Polymer Science and Technology*, **11**, pp. 601-625.
3. X.-D. Hu, S.E. Jenkins, B.G. Min, M.B. Polk, and S. Kumar, *Macromol. Mater. Eng.*, **288**(11), 823-842 (2003).
4. M.G. Northolt and J.J.M. Baltussen, *J. Appl. Polym. Sci.*, **83**, 508-538 (2002).
5. T. Kitagawa, H. Murase and K. Yabuki, *J. Polym. Sci. B: Polymer Physics*, **36**, 39-48 (1998).
6. T. Kitagawa and K. Yabuki, *J. Appl. Polym. Sci.*, **80**, 1030-1036 (2001).
7. R. J. Young, R.J. Day, and M. Zakikhani, *J. Mater. Sci.*, **25**, 127 (1990).
8. http://www.toyobo.co.jp/e/seihin/kc/pbo/pdf/Attachment_1970KB.pdf
9. E. Orndoff, *NASA Technical Memorandum 104814*, Sept. 1995.
10. Y.-H. So, S.J. Martin, K. Owen, P.B. Smith, and C.L. Karas, *J. Polym. Sci. A: Polymer Chemistry*, **37**, 2637-2643 (1999).
11. E.G. Breusova, R.T. Kuznetsova, T.N. Kopylova, and S.V. Nikolaev, *High Energy Chemistry*, **32**(4), 247-250 (1998).
12. H. Ito and K. Ichimura, *Macromol. Chem. Phys.*, **199**, 2547-2551(1998).
13. P.H. Kasai and D. McLeod Jr., *J. Am. Chem. Soc.*, **95**, 4801 (1973).
14. B. Dickens in *Service Life Prediction Methodology and Metrologies*, J.W. Martin and D.R. Bauer, eds., (American Chemical Society, 2001).
15. C.C. Chau, J. Blackson, and J. Im, *Polymer*, **36** (13), 2511-1517 (1995).
16. Y. Cohen and E.L. Thomas, *Macromolecules*, **21**, 433-435 (1988).
17. J.H. Greenwood and P.G. Rose, *J. Mater. Sci.*, **9**, 1809-1814 (1974).
18. C.C. Chau, M.H. Thomsen, and V.L. St. Jeor, *J. Mater. Sci.*, **27**, 5645-5652 (1992).
19. K. Tamargo-Martinez, S. Villar-Rodil, J.I. Paredes, A. Martinez-Alonso, J.M.D. Tascon, and M.A. Montes-Moran, *Macromolecules*, **36**, 8662-8672 (2003).
20. S.J. Krause, T.B. Haddock and D.L. Vezie, P.G. Lenhert, W.-F. Hwang, G.E. Price, T.E. Helminiak, J.F. O'Brien and W.W. Adams, *Polymer*, **29**, 1354-1364 (1988).
21. R.J. Young, R.J. Day, M. Zakikhani, *J. Mater. Sci.*, **25**, 127-136 (1990).
22. T. Kuroki, Y. Tanaka, T. Kohudoh, K. Yabuki, *J. Appl. Polym. Sci.*, **65** (5), 1031-1036 (1996).

23. W.M. Riggs and M.J. Parker, "Surface Analysis by X-ray Photoelectron Spectroscopy", in *Methods of Surface Analysis*, A.W. Czanderna, ed., Elsevier, 1975.
24. NIST XPS database, <http://srdata.nist.gov/xps>.
25. H.H. Willard, L.L. Merrit, Jr., J.A. Dean, and F.A. Settle, Jr., *Instrumental Methods of Analysis*, 7th ed., Wadsworth, Inc., 1988.
26. X. Hu and A.J. Lesser, *Proceedings of the American Chemical Society Meeting, Division of Polymeric Materials, Science and Engineering*, **227**, U562 (2004).
27. N. Sanjeeva Murthy and Franz Reidinger, "X-Ray Analysis", in *A Guide to Materials Characterization and Chemical Analysis*, J.P. Sibilia, ed. (VCH Publishers, Inc., New York, 1996).
28. D.C. Martin and E.L. Thomas, *Macromolecules*, **24**, 2450-2460 (1991).
29. R.J. Davies, M.A. Montes-Moran, C. Riekel and R.J. Young, *J. Mater. Sci.*, **28**, 2105-2115 (2003).
30. K. Tamargo-Martinez, S. Villar-Rodil, J.I. Paredes, A. Martinez-Alonso, and J.M.D. Tascon, *Chem. Mater.*, **15**, 4052-4059 (2003).
31. W.-Y. Yeh and R.J. Young, *Polymer*, **40**, 857-870 (1999).
32. K. Tashiro, H. Hama, J.-I. Yoshino, Y. Abe, Tooru Kitagawa, and K. Yabuki, *J. Polym Sci B: Polym. Phys.*, **39**, 1296-1311 (2001).
33. J.-H. Chang, K. M. Park, S.-M. Lee, and J.B. Oh, *J. Polym. Sci. B.*, **38**, 2537-2545 (2000).
34. E.I. Yoo, A.J. Gavrin, R.J. Farris, and E.B. Coughlin, *High Performance Polymers*, **15**, 519-535 (2003)
35. T. Kubota and R. Nakanishi, *Polymer Letters*, **2**, 655-659 (1964).
36. G. Brana, E. Castellucci and M. Ginanneschi, *Spectrochimica Acta*, **23A**, 751-758 (1967).
37. H. Ito and K. Ichimura, *Macromol. Chem. Phys.*, **199**, 2547-2551 (1998).
38. E.G. Breusova, R.T. Kuznetsova, T.N. Kopylova, and S.V. Nikolaev, *High Energy Chemistry*, **32** (4), 247-250 (1998).
39. P.F. Jackson, K.J. Morgan, and A.M. Turner, *J. Chem Soc., Perkin Transactions II*, **2**, 1582-1587 (1972).
40. Y. Termonia, P. Meakin, and P. Smith, *Macromolecules*, **18**, 2246-2252 (1985).
41. M.-C. G. Jones and D.C. Martin, *Macromolecules*, **28**, 6161-6174 (1995).

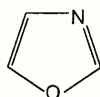
APPENDIX A

SELECTED LITERATURE ON THE HYDROLYTIC STABILITY OF SIMPLE OXAZOLES, BENZOXAZOLES, AND THEIR OXAZOLIUM SALTS

A1. INTRODUCTION

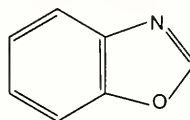
This Appendix provides an overview of selected literature on the hydrolytic stability of simple (i.e., monomeric) oxazoles, benzoxazoles, and their derivatives including oxazolium salts. The chemical structures of oxazole (1) and benzoxazole (2) are shown below. The overview focused on the susceptibility of oxazoles and benzoxazoles to react nucleophilically with water under acidic, alkaline, or neutral conditions resulting in ring fission (i.e., ring opening or cleavage) to yield acyclic products. Under some hydrolytic conditions, the acyclic product(s) may undergo further hydrolysis. Additionally, nucleophilic attack with agents other than water (e.g., ammonia and amines) can also result in ring fission that may be accompanied by a subsequent ring closure reaction of the acyclic product to form a new heterocyclic compound. Nucleophilic attack of oxazoles and benzoxazoles with agents other than water were beyond the scope of this overview. In developing the overview, it was found that few research papers have been published on hydrolytic stability relative to the extent of the oxazole or benzoxazole literature. For example, a number of reviews have been published, but their authors have generally devoted little direct attention to hydrolysis. Moreover, many of these reviews provide only qualitative observations on oxazole or benzoxazole hydrolytic stability; few studies elucidate the kinetics and mechanisms of these hydrolytic degradations.

Oxazole



(1)

Benzoxazole



(2)

The overview concentrates on papers written in English, although the results of many of the early studies on oxazole and benzoxazole chemistry were reported in German. In these cases, the salient points on hydrolytic stability have been included in various

general review articles and textbooks written over the years. It is these reviews and texts that form much of the basis of the current overview. Note that many of these reviews and texts emphasize the oxazole literature and, in some cases, center only on oxazole chemistry without reference to benzoxazole chemistry.

The literature indicates that oxazoles and benzoxazoles are both susceptible to hydrolytic degradation. The degree of susceptibility varies with temperature, pH, catalysis, and the specific chemical structures of the reactant oxazoles and benzoxazoles. Some of the cited information is contradictory. Such contradictions are at times not pointed out in the literature, since often authors have not discussed their findings in relation to the past findings of other authors. It is clear from the literature that the hydrolytic stabilities of oxazoles and benzoxazoles are not equivalent, and that benzoxazoles are seen as being more hydrolytically susceptible.

A2. OXAZOLES

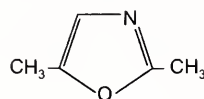
Several major reviews on oxazole chemistry have been published during the last 50 years [1-10]. The earliest review was written by Wiley [1] who covered over a half century of oxazole chemistry from its formative years through the mid-1940s. Wiley's review was followed in 1957 by that of Cornforth [2]. Next came Lakhan and Ternai's review [4] in 1974, which appeared just shortly before that of Turchi and Dewar [5] in 1975. Turchi later published two other reviews in the 1980s [6,8]. Palmer and Venkatraman [10] provided the most recent review in 2003.

Wiley [1] described oxazoles as thermally stable compounds that vary from extremely volatile liquids to those which boil undecomposed at remarkably high temperatures (e.g., 220 °C to 260 °C). However, oxazole reactivity under hydrolytic conditions could not be so simply characterized. He opined that straightforward statements as to whether oxazoles were or were not susceptible to hydrolysis were not possible, and provided examples showing both types of behavior. He attributed the variable hydrolytic stability

of different oxazoles to the nature of the substituents in the oxazole ring. His text implied that, at the time of his review, oxazoles were considered to be susceptible to hydrolysis. He cautioned his readers against such generalizations (that were apparently given in some then-current textbooks) that the oxazole ring readily undergoes fission by acid hydrolysis. In support of his cautionary position, he noted that oxazoles are prepared under aqueous acid conditions, and that many can be successfully steam distilled. He also provided examples of transformations of oxazole derivatives that were carried out in the presence of acids without ring fission. As one of many examples, he cited the nitration of phenyloxazoles with concentrated and dilute nitric acid to yield nitrophenyloxazoles. In the extreme, Wiley considered that some oxazoles are “remarkably stable to aqueous acids.” Noted examples were the quantitative recovery of 2,5-dimethyloxazole (**3**) after treatment with 15 % hydrochloric acid at 100 °C for 6 h, and lack of degradation of 2,5-diphenyloxazole (**4**) by strong hydrochloric acid after several hours at 150 °C. He summarized his findings on hydrolytic stability by stating that, rather than indicating facile oxazole hydrolysis, the literature evidence indicated “a considerable resistance towards acids.”

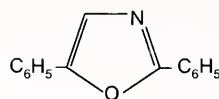
However, as also shown by Wiley’s review [1], this “resistance towards acids” is not universal to all oxazoles. A number of examples were given wherein oxazoles underwent ring fission in acidic conditions, although in many of these cases the hydrolyses were performed at temperatures of 100 °C or greater. Those oxazoles most easily hydrolyzed by acid were stated to be the 5-alkoxyoxazoles. Of the group of 5-alkoxyoxazoles discussed, the most readily hydrolyzed was 2-methyl-5-ethoxyoxazole (**5**). An aqueous solution of its hydrochloride (formed from the oxazole and hydrochloric acid) was reported as completely hydrolyzed after standing 3 d at room temperature. Overall, the number of examples cited wherein oxazoles were shown to be susceptible to hydrolysis was less than the number of examples of oxazoles found to be resistant to hydrolysis.

2,5-dimethyloxazole



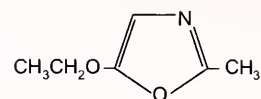
(3)

2,5-diphenyloxazole



(4)

2-methyl-5-ethoxyoxazole

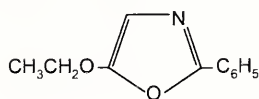


(5)

Cornforth's review [2] complemented that of Wiley [1] and provided additional examples of oxazoles that were and were not hydrolyzed by aqueous acid. In discussing stability, Cornforth noted that the oxazole ring, as formulated, contains an imino ether group and an enol ether group, both of which, when isolated, are exceptionally easily hydrolyzed. He further commented that most oxazoles show a stability, particularly to hydrolysis and to nucleophilic reagents in general, which is quite uncharacteristic of either of these component groups. This stability was explained by assuming that the imino ether and enol ether groups stabilize each other by an interaction involving dipolar forms and resulting in the "non-localization" of six π -electrons. Cornforth also considered that the state-of-knowledge regarding hydrolytic stability was such that information was not available to define the conditions necessary to degrade alkyloxazoles, and that the mechanism of acid hydrolysis of oxazoles was unknown at the time.

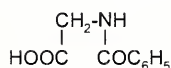
In providing examples of oxazole hydrolysis, Cornforth again noted the hydrolytic susceptibility of 5-alkoxyoxazoles. He cited that 2-phenyl-5-ethoxyoxazole (6) on warming (temperature not specified) with dilute hydrochloric acid is converted to hippuric acid (7) and ethanol (8). He also cited that 2-amyl-5-ethoxyoxazole (9) is rapidly converted to ethyl hexanamidoacetate (10) by dilute hydrochloric acid at room temperature, but that the more heavily substituted alkoxyoxazoles are less readily hydrolyzed. He also noted that 5-aminoxazoles appear to be readily hydrolyzed by acid, although in the example cited, the hydrolysis was performed at elevated temperatures. In contrast, 2-aminoxazoles were considered to be somewhat stable to acid hydrolysis.

2-phenyl-5-ethoxyoxazole



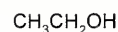
(6)

hippuric acid



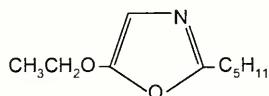
(7)

ethanol



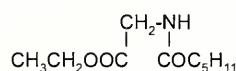
(8)

2-amyl-5-ethoxyoxazole



(9)

hexanamidoacetate



(10)

In contrast to their discussions on the reactivity of oxazoles under acidic conditions, both Wiley [1] and Cornforth [2] simply reported with little comment that oxazoles were stable to alkali. Cornforth further noted that this alkaline resistance had been observed in the cases of the 5-alkoxyoxazoles. Lakhan and Ternai [4] echoed this view of stability to alkali. Interesting, they also mentioned without discussion the stability of oxazoles toward acids and ring fission as demonstrated by their preparation under acidic conditions. They made no mention that some oxazoles were known to be cleaved by acid hydrolysis.

The 1975 review by Turchi and Dewar [5] provided little additional information on the acid hydrolysis of oxazoles from that given in previous reviews. In fact, these authors acknowledged that nucleophilic ring openings were extensively discussed by Wiley [1] and Cornforth [2], and stated that most of the available data concerning reactions of oxazoles with acids had been discussed by them. Furthermore, ring fission through acid hydrolysis was not a topic specifically addressed by Turchi in his two '80s reviews [6,8], although in 1986 he reiterated the proclivity of 5-alkoxyoxazoles and 5-aminooxazoles to undergo facile ring fission when treated with aqueous acid. However, it was apparent from Turchi's reviews that the utility of reactions involving oxazole ring fissions were finding increased utility in synthetic

organic chemistry. In 1986, Turchi wrote [8] that “one of the most intriguing aspects of heterocyclic chemistry is the conversion of one heterocyclic system to another. Most of these processes occur via ring opening of the heterocycle under acidic, basic, thermal, or photochemical conditions followed by recyclization of an acyclic intermediate. The reactivity of oxazoles toward acids, bases, heat, and dienophiles make them a particularly attractive and useful starting point for a variety of ring transformations.” This statement along with the examples given provides additional supporting evidence of the susceptibility of some oxazoles to hydrolysis under acidic and even alkaline conditions. This utility of ring-opening reactions such as hydrolysis to generate new heterocyclic systems was again reported by Palmer and Venkatraman [10], who provided numerous examples of such synthetic pathways.

The reviews mentioned above generally define the overall state-of-knowledge regarding oxazole reactivity under hydrolytic conditions. In addition to these reviews, many authors have published papers or provided comments in textbooks that include specific statements on, or examples of, the phenomenon. Many of these are cited in the paragraphs that follow.

Karrer's early organic chemistry textbook [11] illustrated pathways for synthesizing oxazoles under acid conditions. He also stated that oxazoles, particularly 2-alkyl (or aryl)-5-alkoxyoxazoles, were decomposed on boiling with acids, although the subject of hydrolysis was not directly discussed nor were examples of hydrolytic degradation reactions given.

Loudon [12] summarized that, although oxazoles possess fair resistance to hydrolysis, ring stability varies considerably depending on the nature of the substituents present. Normally the ring is stable to alkali, but it is sometimes hydrolyzed by hot concentrated acids.

Albert [13,14] reported that oxazoles are highly resistant to alkali, and with certain exceptions, to acid. He cited the examples given by others that 2,5-dimethyloxazole (**3**)

is unchanged by heating for several hours at 100 °C with hydrochloric acid, whereas 5-ethoxy- and 5-amino-oxazoles are hydrolyzed by dilute acids.

Bredereck et al. [15] described the ring opening of a number of oxazoles in aqueous acidic or methanolic-acidic 2,4-dinitrophenylhydrazine (2,4-DNP). The authors proposed a reaction sequence in which the first step was the hydrolytic ring opening of a nitrogen-protonated oxazole. The resultant acyclic intermediate then reacted with the 2,4-DNP to yield the final product. Reactions were conducted at both reflux temperatures for unspecified times and at room temperature over periods of about 2 weeks to 6 weeks. The room temperature reactions achieved relatively low yields in comparison to those obtained at reflux temperatures.

Badger [16] indicated that oxazoles, which he considered to be aromatic systems, display only moderate stability of the ring system. With some seeming contradiction, he further commented that they are generally stable to alkali, and have some degree of stability to acid hydrolysis. The stability was described as varying with the nature of substituents. As an example of unstable oxazoles, he reiterated that 5-alkoxyoxazoles are readily hydrolyzed by acid.

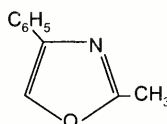
Acheson [17] stated that oxazoles are stable to concentrated acids at moderate temperatures, but that high temperatures (not specified) sometimes result in ring fission. He also mentioned that oxazoles are stable to alkali.

Katritzky and Lagowski [18] made a general statement without discussion or example that oxazoles give acylaminoketones under acid conditions. They also commented that oxazoles are resistant to alkali.

Palmer [19], in a simple statement, indicated that the oxazole ring is often decomposed by hot and strong acids.

Joule and Smith [20] described oxazoles (and the other 1,3-azoles, imidazoles and thiazoles) as being quite stable even in strong acid under vigorous conditions (not specified). They also commented that oxazoles are stable to alkalis under vigorous conditions, citing as an example that 2-methyl-4-phenyl oxazole (**11**) is recovered unchanged from exposure to potassium hydroxide in ethanol at 200 °C.

2-methyl-4-phenyl oxazole



(11)

Campbell [21] summarized that oxazoles are resistant to alkaline hydrolysis, but readily undergo ring fission by acids to acylaminoketones, probably because of N-protonation that enhances the susceptibility of the ring to nucleophilic attack. In a somewhat contradictory statement, he also indicated that many oxazoles are soluble in acids without fission, although these can be made under some conditions (e.g., hot strong acids) to give acylaminoketones.

Boyd [22] indicated that oxazole has little aromatic character and, consequently, oxazole chemistry is dominated by its tendency to undergo ring fission rather than preserve its intact ring system. Simple oxazoles resist attack by alkali and other nucleophilic reagents under mild conditions, but at elevated temperatures the ring is cleaved.

Gilchrist [23] wrote that oxazole can be regarded as aromatic, although bond-length data indicate that the bonding is somewhat localized. He indicated that this reduced aromaticity (associated with incomplete delocalized bonding) of the oxazole ring system should not be equated with instability. As evidence, he offered that some diaryloxazoles are extremely stable to heat and have been recovered unchanged after heating to 400 °C. He did not discuss ring-fission hydrolytic reactions.

Hassner and Fischer [24] indicated that nucleophilic attack on the neutral oxazole ring takes place only with difficulty, either at elevated temperatures (over 180 °C) or in the presence of electron withdrawing substituents. On the other hand, protonated oxazoles react with nucleophiles, leading to ring fission.

Eicher and Hauptman [25] summarized that the electronegativity of the oxazole nitrogen atom causes the π -electron density of the ring to be low, especially on the C-2 atom. Thus, reaction with nucleophiles should occur in the 2-position, which is known to occur even if a substituent is present in that position. Ring fission takes place and, depending on the nucleophilic reagent, may in turn be followed by ring closure.

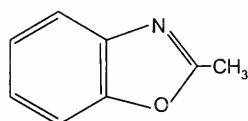
Joule, Mills and Smith [26] repeated that oxazoles (as well as imidazoles and thiazoles) undergo reactions with nucleophilic reagents in which the heterocyclic ring undergoes fission. Examples given were for oxazole reactions with phenylhydrazine and formamide. No example of oxazole hydrolysis was included in their summary.

A3. BENZOXAZOLES

A review of benzoxazole chemistry was given by Cornforth [27] in 1957. Much of the subject matter was devoted to benzoxazole syntheses with some attention given to hydrolysis. Cornforth summarized that the benzoxazoles have considerable thermal stability, but that they undergo hydrolysis under both acidic and alkaline conditions. He also commented that this hydrolysis, described as occurring with “relative ease,” had been recognized from the first years of benzoxazole chemistry. He cited Ladenburg [28], who found in 1876 that 2-methylbenzoxazole (**12**) on heating with water, or more rapidly with dilute acid, gave o-acetamidophenol (**13**). 2-Phenylbenzoxazole (**14**) needed more vigorous conditions (hydrochloric acid at 130 °C), and the products were benzoic acid (**15**) and o-aminophenol (**16**). Both acidic and alkaline hydrolyses were depicted as being reversible reactions with alkaline hydrolysis not as facile as acidic hydrolysis. Regarding the hydrolytic mechanism, he stated that such reactions are clearly nucleophilic attack on

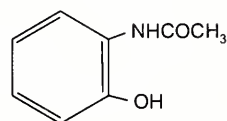
C-2 position of benzoxazole rings, and that it seems probable that hydroxyoxazolines are intermediates. As evidence, he cited Skraup [29], who examined the effect of substituents in the C-2 position on the rate of acid hydrolysis. The substituent allowing the most rapid hydrolysis was hydrogen; then in order of increasing difficulty became benzyl, ethyl, methyl, m-nitrophenyl, benzoyl, phenyl, p-methoxyphenyl, b-naphthyl, a-naphthyl, o-hydroxyphenyl, and p-nitrophenyl.

2-methylbenzoxazole



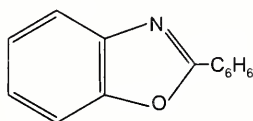
(12)

o-acetamidophenol



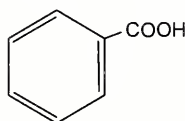
(13)

2-phenylbenzoxazole



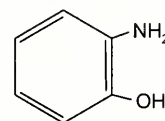
(14)

benzoic acid



(15)

o-aminophenol



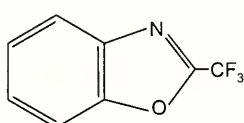
(16)

Note that Cornforth's description of benzoxazole hydrolysis as occurring with "relative ease" contrasts with his depiction of oxazole hydrolysis. As mentioned in Sec. A2, Cornforth [2] summarized that most oxazoles show stability to hydrolysis and to nucleophilic reagents in general. Consistent with Cornforth's reviews indicating differing chemistries for oxazoles and benzoxazoles, Boyd [22] commented without discussion that "the chemistry of benzoxazole differs from that of oxazole in many respects." Many examples of the benzoxazole hydrolytic instability have been given in the literature and are cited in the paragraphs that follow.

Jackson, Morgan, and Turner [30] reported on the kinetics of benzoxazole hydrolytic degradation under acid conditions in 1972. The hydrolysis was considered to be a facile reaction, which was attributed to a low aromatic stability of the oxazole ring system. They noted that the hydrolytic process may proceed by nucleophilic attack on the polar

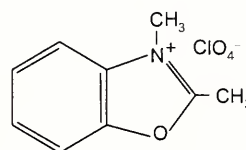
CN (i.e., carbiminy) bond. This results in 2-hydroxybenzoxazoline, which had been suggested by Skraup and Moser [31]. The benzoxazoles included in the Jackson et al. study were the parent compound (**2**), 2-methylbenzoxazole (**12**), and 2-phenylbenzoxazole (**14**), 2-trifluoromethylbenzoxazole (**17**), and 1,2-dimethylbenzoxazolium perchlorate (**18**). The reactions were mostly studied at 25 °C in aqueous media over the pH range of 1.5 to 5. In general the corresponding amide was detected as the initial hydrolysis product.

2-trifluoromethylbenzoxazole



(17)

1,2-dimethylbenzoxazolium perchlorate



(18)

In water, benzoxazole and 2-methylbenzoxazole displayed peak rate constants at a pH of 0.35 and pH of 1.35, respectively (Figure 1). For a given pH, benzoxazole peak rate constants were greater than those for 2-methylbenzoxazole. For both compounds, the hydrolysis reactions showed acid catalysis for solutions of low acidity but retardation at higher acidities. 2-Phenylbenzoxazole was insufficiently soluble for direct study in water; in 80 % aqueous methanol, it was about 100 times less reactive than 2-methylbenzoxazole. Mechanisms were proposed and rate expressions were derived for the hydrolyses.

Illustrating the effect of substituents on ring stability, the rate behavior for 2-trifluoromethylbenzoxazole was seen to be different from that for benzoxazole and 2-methylbenzoxazole (Figure 2). Specifically in the case of 2-trifluoromethylbenzoxazole, the rate was constant over the pH range of 2 to 5, whereas at lower pHs, it increased as the acidity increased.

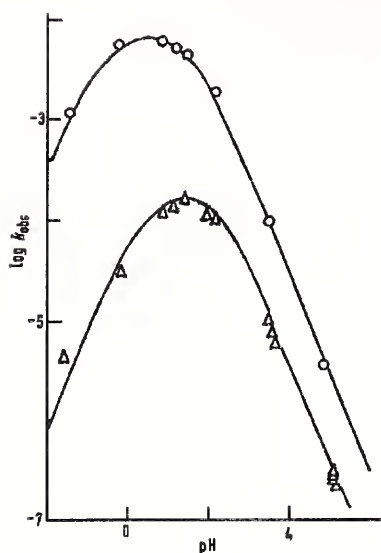


Figure 1. Rate versus pH for the hydrolysis of benzoxazole (o) and 2-methylbenzoxazole (Δ) (from Jackson et al. [30]).

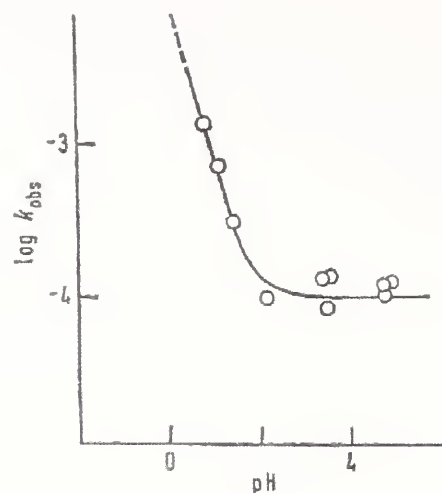
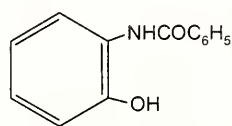


Figure 2. Rate versus pH for the hydrolysis of 2-trifluoromethylbenzoxazole (from Jackson et al. [30]).

Kulagin et al. [32] reported on the kinetics and mechanism of the hydrolysis of 2-phenylbenzoxazole (**14**) and o-benzamidophenol (**19**), which were studied as model compounds of cyclized and non-cyclized fragments of polybenzoxazoles. The authors quote Phillips [33] that when 2-phenylbenzoxazole is heated in aqueous solutions of mineral acids, o-benzamidophenol is first formed. In turn, the o-benzamidophenol can be re-converted to the 2-phenylbenzoxazole or further hydrolyzed to o-aminophenol and benzoic acid under the reaction conditions studied. The kinetics of the decomposition were followed at four temperatures ranging from 100 °C to 150 °C for five acid concentrations. Activation energies were found to be practically independent of acid concentration over the concentration range selected. The effective rate constant for the hydrolysis of 2-phenylbenzoxazole was seen to decrease with increasing acid concentration. It is interesting to note that Kulagin et al. did not cite Jackson et al. [30], who also studied the acid-hydrolysis kinetics of 2-phenylbenzoxazole.

o-benzamidophenol

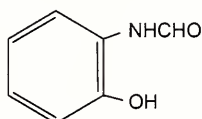


(**19**)

Phillips [33] discussed benzoxazole hydrolysis in conjunction with his attempts to convert amino-2-methylbenzoxazoles into the corresponding arsinic acids*. He stated that benzoxazoles in general are very unstable to hydrolytic reagents. Key compounds in his study were nitro-2-methylbenzoxazoles and amino-2-methylbenzoxazoles. He found that the nitro-systems were very unstable to cold mineral acids or cold caustic alkalis. For example, the 5- and 7-nitro-derivatives were hydrolyzed even by hot water (i.e., no acid present). On the other hand, the 4- and 6-nitro-derivatives showed more stability as they could be crystallized from hot water containing a little acetic acid. The amino systems were described as more stable to hot water, with only the 4-amino-derivative being appreciably decomposed. All amino-derivatives were unstable to warm acids and alkalis. For both the nitro-amino-systems, the products of hydrolysis were derivatives of o-aminophenol.

Albert, Goldacre, and Phillips [34] studied the strength of some heterocyclic bases using potentiometric titration. Attempts to measure benzoxazole by titration at 20 °C with dilute acid were unsuccessful, as it decomposed to 2-formamidophenol (**20**) too rapidly [13,14,34].

2-formamidophenol



(**20**)

Seyhan and Avan [35] described an investigation to oxidize certain heterocycles having active methyl groups with selenium dioxide. The intended products were corresponding aldehydes. In the case of 2-methylbenzoxazole (**12**), neither the aldehyde nor the acid were obtained, because the oxazole ring was cleaved producing o-acetamidophenol (**13**).

* Phillips' paper uses an older numbering system for benzoxazoles. As a result, he refers to the compounds under study as "amino-1-methylbenzoxazoles" [33].

Loudon [3] summarized that benzoxazoles may be opened by hot mineral acids or fusion with alkali. He further stated that benzoxazole itself is hydrolyzed by prolonged boiling with water and, more readily, by dilute acid forming o-formamidophenol (**20**) or o-aminophenol (**16**).

Albert [13,14] stated that many benzoxazoles are hydrolyzed to their starting materials (i.e., a ring fission occurs) with hot water or cold, dilute mineral acid. This statement contrasts with his description mentioned above that, with certain exceptions, oxazoles are highly resistant to acids.

Acheson [17] tersely stated that benzoxazole is readily hydrolyzed by boiling water or dilute acids.

Goetz and Rathburn [36] prepared 2-methylbenzoxazole (**12**) by refluxing o-aminophenol (**16**) in acetic anhydride. They reported that, a few months after the preparation, a white solid was observed in the liquid 2-methylbenzoxazole. Upon isolation by filtering, the solid was shown to be the hydrolysis product, o-acetamidophenol (**13**). When the white solid was filtered from the 2-methylbenzoxazole using a wet filter, the filtered 2-methylbenzoxazole reacted in a few hours to form more of the o-acetamidophenol in abundance.

Soloski, Moore, and Tamborski [37] examined the relative hydrolytic stability of a number of 2- and 2,5-perfluoroalkyl and perfluoroalkylether substituted benzoxazoles (as well as benzothiazoles) for use in polymers having potentially improved hydrolytic stability. The hydrolysis reactions were conducted in anhydrous tetrahydrofuran (THF) with H₂O, NH₄OH, CH₃COOH, or HF generally at 100 °C for a week, although some of the NH₄OH and HF tests were sufficiently fast that those reactions were also conducted at 22 °C. The nature of the hydrolytic degradation products was not discussed. Among the findings, they reported that all compounds studied were stable to H₂O and CH₃COOH hydrolysis. It was also reported that the non-branched substituted benzoxazoles were unstable to NH₄OH and HF hydrolysis, although the α -branched benzoxazoles offered

increased hydrolytic stability to NH_4OH and HF , which was attributed to steric hindrance.

Hegedus et al. [38] reported on the synthesis of a number of 2,5-disubstituted 3,6-diamino-1,4-benzoquinones. In these syntheses, benzobis(oxazoles) were at times used as protecting groups, which were in turn removed by hydrolysis. In discussions providing the rationale for use of such protecting groups in the syntheses undertaken, the authors stated that “simple benzoxazoles hydrolyze readily.” A feature of a good protecting group is that it be readily removed when no longer needed.

Zaikov and Necaev [39] gave a brief summary of the acidic-alkaline hydrolysis and degradation kinetics of heterochain polymers (e.g., amides, anilides, esters, imides, benzoxazoles, benzoxazinones) from the viewpoint of reclaiming monomers from such polymers. Regarding breakdown of benzoxazole, they showed a two-step hydrolytic degradation of 2-phenylbenzoxazole (**14**) that produced o-aminophenol (**16**) and benzoic acid (**15**) through an intermediate, o-benzamidophenol (**19**)^{*}. Over a sulfuric acid range of 10 % to 70 %, the rate of hydrolysis went through a maxima with the most rapid occurring at an acid concentration of about 20 %. A general kinetic rate equation was given. Zaikov and Necaev also developed rate constant data for the hydrolysis of 2-phenylbenzoxazole in the presence of about 2 % to 12 % potassium hydroxide. A general kinetic rate equation for this alkaline hydrolysis was also given. The authors demonstrated that, for the conditions compared, 2-phenylbenzoxazole hydrolyzed faster in the alkaline medium than in the acid medium.

Ono et al. [39] described the preparation of 4-(aryloxy)-5-nitro-2-aminophenols. A proposed step in the synthesis involved the hydrolysis of substituted benzoxazoles used as a protecting groups. In investigating the synthetic pathway, it was found that acid hydrolysis of a number of 2-substituted t-butyl benzoxazoles failed; however, alkaline (KOH) hydrolysis in refluxing ethanol of these compounds gave the corresponding aminophenol derivatives. The authors described this pH dependence as “unexpected.”

^{*} Zaikov and Necaev [39] referred to this product as o-benzoylaminophenol.

Thus, they conducted a follow-up experiment to estimate rate constants for the hydrolytic cleavage of model benzoxazoles (2-methyl, 2-t-butyl, 6-nitro-2-methyl, & 6-nitro-2-t-butyl) to amidophenols and aminophenols. The kinetic measurements were performed in buffered 50 % aqueous 2-propanol over the pH range of 2.5 to 12.5 at a temperature of 80 °C. At high pH, each of the two 6-nitro-compounds was considerably faster than its counterpart without a nitro group.

Werstiuk and Ju [41] reported on the protium-deuterium exchange of benzo-substituted heterocyclics in neutral D₂O at elevated temperatures. 2-Methylbenzoxazole (**12**) was found to undergo facile hydrolysis at 115 °C to 2-acetamidophenol (**13**) with incorporation of deuterium into the methyl group. The hydrolysis was described as faster than the deuterium exchange.

Dey and Dogra [42] studied the absorption and fluorescence characteristics of some 2-alkyl and 2-aryl-benzoxazoles in different solvents and at various acid concentrations. Aqueous solutions having pH values less than 1 to more than 13 were among those used for the measurements. Included among the compounds were benzoxazole (**2**), 2-methylbenzoxazole (**12**), and 2-phenylbenzoxazole (**14**). In describing the experiments, they commented that, to avoid hydrolysis, the solutions were prepared just before the measurements. They further commented that no changes in the absorption spectra were observed over the course of the measurements (presumably implying that hydrolysis did not occur during the course of the measurements).

Döpp and Döpp [43] provided a review that centered on the syntheses of benzoxazoles, although a few comments were made regarding transformations that they undergo. They indicated with supporting literature citations that benzoxazole undergoes ring fission under mild hydrolysis to 2-aminophenols, and that this cleavage is of synthetic importance in individual cases.

de Raadt et al. [44] also used benzoxazoles as protecting groups in syntheses, as they could be readily removed from the compound of interest. They found that a viable

medium for removal was refluxing (for several hours) in aqueous alcohol (methanol or ethanol) with aqueous hydrochloric acid and zinc chloride. The reaction was described as proceeding through the benzoxazole-ring opened amide (i.e., acylaminophenol or amidophenol) that was further hydrolyzed to the desired product.

Kolenc, Kocevar, and Polanc [45] investigated the use oximes as synthetic reagents for insertion of a CH moiety into a molecule. In that regard, they reacted (refluxing anhydrous ethanol for about 30 h) certain oximes with o-aminophenol. Among the products, they obtained benzoxazole (**2**) and also 2-formamidophenol (**20**). They postulated that the 2-formamidophenol arose from the hydrolysis of the intermediate, an o-dialkoxymethylaminophenol, which was supposedly the first product of the reaction of the oxime with the o-aminophenol. The water necessary for that hydrolysis was postulated as being present to a small extent in the ethanol. It was interesting to note that they also postulated that the 2-formamidophenol did not result from hydrolysis of benzoxazole, because such hydrolysis was considered unlikely under neutral conditions.

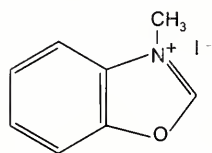
A4. OXAZOLIUM AND BENZOXAZOLIUM SALTS

As evidenced from the literature reviewed, alkylated salts formed from either simple oxazoles or benzoxazoles are generally quite susceptible to hydrolytic ring fission. This section of the Appendix presents a summary of these findings from the literature reviewed.

Clark [46] studied the hydrolysis of a number simple benzoxazolium salts including benzoxazole methiodide (**21**), 2-methylbenzoxazole methiodide (**22**), and 2-phenylbenzoxazole methiodide (**23**). He concluded that the benzoxazolium salts are hydrolyzed by water alone. For example, 2-methylbenzoxazole methiodide gave a partial yield of o-acetylmethylaminophenol (**24**) after 8 h in aqueous solution at room temperature after 8 h; the salt was completely hydrolyzed after 66 h under the same conditions. Additionally, when dissolved in warm water (temperature not specified), 2-phenylbenzoxazole methiodide immediately yielded o-benzoylmethylaminophenol

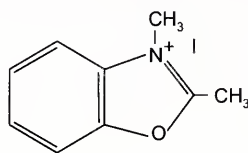
(25). Benzoxazole methiodide yielded o-formylmethylaminophenol (26) when reacted in an aqueous alkaline aqueous solution.

benzoxazole methiodide



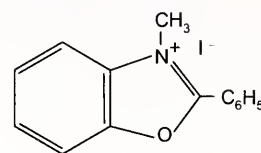
(21)

2-methylbenzoxazole methiodide



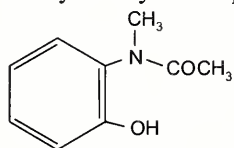
(22)

2-phenylbenzoxazole methiodide



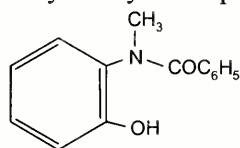
(23)

o-acetylmethylaminophenol



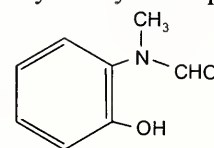
(24)

o-benzoylmethylaminophenol



(25)

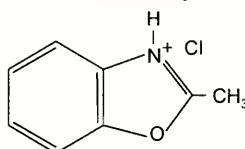
o-formylmethylaminophenol



(26)

In his study of amino-2-methylbenzoxazoles, Phillips [33] prepared 2-methylbenzoxazole hydrochloride (27). This compound was described as being readily hydrolyzed by cold water. Further details including identification of the hydrolysis product(s) were not given.

2-methylbenzoxazole hydrochloride

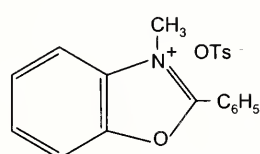


(27)

Ott, Hayes, and Kerr [47] studied the hydrolysis of a number of 2,5-disubstituted-3-methyloxazolium salts. They found that in acidic solution the oxazolium salts studied were quite stable, as evidenced by their being only slightly decomposed by refluxing for 8 h with 48 % hydrobromic acid. In dilute base, however, these oxazolium salts were rapidly and quantitatively converted at room temperature to the N-methyl-a-acylamido ketone by hydrolytic ring fission. The resulting amides could be further hydrolyzed with

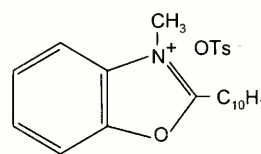
acid to N-methyl-a-amino ketones, whereas the oxazoles themselves were not subject to such facile hydrolysis. The study also included two benzoxazolium salts, 2-phenyl-3-methylbenzoxazolium tosylate (**28**) and 2-(1-naphthyl)-3-methylbenzoxazolium tosylate (**29**). These benzoxazolium salts were described as being more readily hydrolyzed than the oxazolium salts. Specifically, after a few minutes of being dissolved in water, either benzoxazolium salt yielded the corresponding o-amidophenol.

2-phenyl-3-methylbenzoxazolium tosylate



(**28**)

2-(1-naphthyl)-3-methylbenzoxazolium tosylate

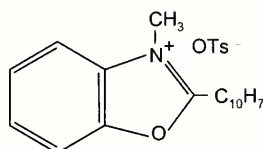


(**29**)

Cornforth [27] concluded from his review of the literature that benzoxazolium salts undergo hydrolytic fission with great ease. Among the evidence supporting his conclusion, he cited Clark's finding [47] that under hydrolysis, 2-phenylbenzoxazole methiodide (**23**) yields o-benzoylmethylaminophenol (**25**).

Loudon [3] cited that benzoxazole methiodide (**21**) is hydrolyzed at 60 °C by 20 % HCl to o-methylaminophenol (**30**).

o-methylaminophenol

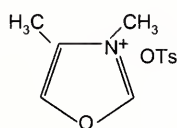


(**30**)

Duclos and Haake [48] compared the stabilities of a number of azolium compounds including 3,4-dimethyloxazolium tosylate (**31**). Reaction rates were determined at 30 °C. It was concluded that the oxazolium ion was unstable at pH near neutrality and

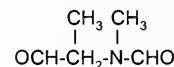
hydrolyzed readily to its ring-opened form, 2-(N-methylformylamino)propanal (**32**). They reported that, at pH 7.4, the half-life of the ring opening reaction was approximately 20 s.

3,4-dimethyloxazolium tosylate



(**31**)

2-(N-methylformylamino)propanal



(**32**)

Campbell [21] commented that quaternary salts of benzoxazole are hydrolyzed much more readily than benzoxazole itself. As evidence, he cited the hydrolysis of benzoxazole methiodide (**21**) to produce o-formylmethylanilino-phenol (**26**).

Boyd [22] summarized that oxazoles and benzoxazoles yield salts with acids, alkyl halides, methyl toluene-p-sulfonate, and similar compounds, while noting that the quaternization can be limited due to steric effects of bulky C-2 substituents. For example, he remarked that 2-phenylbenzoxazole does not react with ethyl iodide even at 240 °C. He also mentioned that simple oxazolium and benzoxazolium salts, such as hydrochlorides and picrates, are unstable and readily hydrolyze, even in air.

Sainsbury [49] indicated that benzoxazoles form salts with acids and are quaternized by heating with alkyl halides. Both types of salts were described as being readily hydrolyzed in aqueous media.

Hassner and Fischer [9] have also stated that protonated oxazoles and oxazolium salts react with nucleophiles leading to ring fission. They did not mention benzoxazolium salts.

Eicher and Hauptman [25] summarized that nucleophiles attack benzoxazoles, benzoxazolium salts and N-alkylbenzoxazolium salts resulting in ring fission

A5. APPENDIX REFERENCES

1. Wiley, R.H., "The Chemistry of the Oxazoles," *Chemical Reviews*, Vol. 37, No. 3 (1945), pp. 401-42.
2. Cornforth, J.W., "Oxazole and Its Derivatives," in *Five-Membered Heterocycles Containing Two-Hetero Atoms and Their Benzo Derivatives*, Ed. R.C. Elderfield, Vol. 5. *Heterocyclic Compounds*, John Wiley & Sons: New York (1957), pp. 298-417.
3. Loudon, J.D., "Compounds Containing a Five-Membered Ring with Two Hetero Atoms: Dioxol and Oxazole Groups and Their Thia Analogues," in *Heterocyclic Compounds*, Ed. E.H. Rodd, Vol. IV, Part A, *Chemistry of Carbon Compounds*, Elsevier Publishing Company: New York (1957), pp. 332-438.
4. Lakhan, R. and B. Ternai, "Advances in Oxazole Chemistry," in *Advances in Heterocyclic Chemistry*, Eds. A.R. Katritzky and A.J. Boulton, Academic Press: New York (1974), pp. 99-211.
5. Turchi, I.J. and M.J.S. Dewar, "The Chemistry of Oxazoles," *Chemical Reviews*, Vol. 75, No. 4 (1975), pp. 389-437.
6. Turchi, I.J., "Oxazole Chemistry - A Review of Recent Advances," *Industrial and Engineering Chemistry Product Research and Development*, Vol. 20, No. 1 (1981), pp. 32-76.
7. Boyd, G.V., "Oxazoles and Their Benzo Derivatives," in *Comprehensive Heterocyclic Chemistry: The Structure, Reactions, Synthesis and Uses of Heterocyclic Compounds*, Ed. C.J. Drayton, Pergamon Press: Oxford (1984), pp. 177-233.
8. Turchi, I.J., "Oxazoles," in *Oxazoles*, Ed. I.J. Turchi, John Wiley & Sons: New York (1986).
9. Hassner, A. and B. Fischer, "New Chemistry of Oxazoles," *Heterocycles*, Vol. 35, No. 2 (1993), pp. 1441-1465.
10. Palmer, D.C. and S. Venkatraman, "Synthesis and Reactions of Oxazoles," in *Chemistry of Heterocyclic Compounds, Oxazoles: Synthesis, Reactions, and Spectroscopy, Part A*, Ed. D.C. Palmer, Wiley-Interscience: Hoboken, NJ (2003).
11. Karrer, P., *Organic Chemistry*, 1938, Elsevier: Amsterdam (1938), pp. 722-723.
12. Loudon, J.D., "Compounds Containing a Five-Membered Ring With Two Hetero Atoms: Dioxol and Oxazole Groups and Their Thia Analogues," in *Heterocyclic Compounds*, Ed. E.H. Rodd, Elsevier Publishing Company: New York (1957), pp. 332-438.
13. Albert, A., *Heterocyclic Chemistry: An Introduction*, Essential Books: Fair Lawn, NJ (1959), p. 211.
14. Albert, A., *Heterocyclic Chemistry: An Introduction*, 2nd ed., The Athlone Press, University of London: London (1968), p. 266.
15. Brederick, H., R. Gompper, F. Reich, and U. Gotsmann, U., "Ringaufspaltung von Oxazolen mit 2,4-Dinitrophenylhydrazin (Ring Opening of Oxazoles with 2,4-Dinitrophenylhydrazine)," *Chemische Berichte*, Vol. 93 (1960), pp. 2010-2015.
16. Badger, G.M., *The Chemistry of Heterocyclic Compounds*, Academic Press: New York (1961), p. 198.
17. Acheson, R.M., *An Introduction to the Chemistry of Heterocyclic Compounds*, Interscience Publishers: New York (1967), pp. 270-284.

18. Katritzky, A.R. and J.M. Lagowski, *The Principles of Heterocyclic Chemistry*, Methuen & Company: London (1967), p. 151.
19. Palmer, M.H., *The Structure and Reactions of Heterocyclic Compounds*, St. Martin's Press: New York (1967), p. 373.
20. Joule, J.A. and G.F. Smith, *Heterocyclic Chemistry*, 2nd ed., Van Nostrand Reinhold Company: London (1978), pp. 305 & 310.
21. Campbell, M.M., "Five-Membered Ring Systems," in *Comprehensive Organic Chemistry, The Synthesis and Reactions of Organic Compounds, Vol. 4, Heterocyclic Compounds*, Ed. P.G. Sammes, Pergamon Press: Oxford (1979), p. 971.
22. Boyd, G.V., "Oxazoles and Their Benzo Derivatives," in *Comprehensive Heterocyclic Chemistry: The Structure, Reactions, Synthesis and Uses of Heterocyclic Compounds*, Ed. C.J. Drayton, Pergamon Press: Oxford (1984), pp. 177-233.
23. Gilchrist, T.L., *Heterocyclic Chemistry*, 2nd ed., John Wiley & Sons: New York (1992), p. 307.
24. Hassner, A. and B. Fischer, "New Chemistry of Oxazoles", *Heterocycles*, Vol. 35, No. 2 (1993), pp. 1441-1465.
25. Eicher, T. and S. Hauptman, *The Chemistry of Heterocycles: Structure, Reactions, Syntheses and Applications*, Georg Thieme Verlag: Stuttgart (1995), pp. 122-133.
26. Joule, J.A., K. Mills, and G.F. Smith, *Heterocyclic Chemistry*, 3rd ed., Chapman & Hall: London (1995), p. 376.
27. Cornforth, J.W., "Benzoxazoles and Related Systems," in *Five-Membered Heterocycles Containing Two-Hetero Atoms and Their Benzo Derivatives*, Ed. R.C. Elderfield, John Wiley & Sons: New York (1957), pp. 419-451.
28. Laudenburg, A., "Condensationsvorgänge in der Orthoreihe (Condensation Reactions in the Ortho Series)," *Berichte*, Vol. 9 (1876), p. 1524.
29. Skraup, S., "Additionsreaktionen und Ringspaltungen Einiger Heterocyclischer Verbindungen. Ein Beitrag zur Lehre von der Valenzlinienverteilung (Addition Reactions and Ring Fission of Some Heterocyclic Compounds. A Contribution to the Theory of the Valence Line Distributions)," *Annalen der Chemie*, Vol. 419 (1919), p. 68.
30. Jackson, P.F., K.J. Morgan, and A.M. Turner, "Studies in Heterocyclic Chemistry. Part IV. Kinetics and Mechanisms for the Hydrolysis of Benzoxazoles," *Journal of the Chemical Society, Perkin Transactions 2: Physical Organic Chemistry* (1972), pp. 1582-1587.
31. Skraup, S. and M. Moser, "Über Benzoxazol-Derivate (Benzoxazole Derivates)," *Berichte*, Vol. 55 (1922), pp. 1080-1101.
32. Kulagin, V.N., T.P. Esakova, K.J. Morgan, A. Zeiser, E.F. Brin, G.M. Tseitlin, and V.V. Korshak, "Hydrolysis of 2-Phenylbenzoxazole and o-Benzamidophenol in Aqueous Solutions of Sulfuric Acid," *Izvestiya Akademii Nauk Gruzii, Seriya Khimicheskaya*, Vol. 8 (1974), pp. 1770-1774.
33. Phillips, M.A., "The Amino-1-Methylbenzoxazoles and Their Conversion into the Arsinic Acids of o-Aminophenol," *Journal of the Chemical Society* (1930), pp. 2685-2690.
34. Albert, A., R. Goldacre, and J. Phillips, "The Strength of Heterocyclic Bases," *Journal of the Chemical Society* (1948), pp. 2240-2249.

35. Seyhan, M. and S. Avan, "The Behavior of Some Heterocyclics Having Active Methyl Groups With Selenium Dioxide," *Revue de la Faculte des Science de L'Universite D'Istanbul*, Vol. 16A (1951), pp. 30-32.
36. Goetz, J.R. and D.W. Rathburn, "Hydrolysis of 2-Methylbenzoxazole to 2-Hydroxyacetanilide", *Texas Journal of Science*, Vol. 24, No. 2 (1972), p. 261.
37. Soloski, E.J., G.J. Moore, and C. Tamborski, "Synthesis of 2- and 2,5-Substituted Benzoxazoles and Benzothiazoles," *Journal of Fluorine Chemistry*, Vol. 8 (1976), pp. 295-304.
38. Hegedus, L.S., R.R. Odle, P.M. Winton, and P.R. Weider, "Synthesis of 2,5-Disubstituted 3,6-Diamino-1,4-Benzoquinones," *Journal of Organic Chemistry*, Vol. 47, No. 13 (1982), pp. 2607-2613.
39. Zaikov, G.E. and P.P. Necaev, "Untersuchungen zu Kinetik und Mechanismus der Hydrolyse von Heterokettenpolymeren zur Rückgewinnung der Monomere (Investigation of Kinetics and Mechanisms of Hydrolysis of Heterochain Polymers for Regeneration of Monomers)," *Acta Polymerica*, Vol. 36, No. 11 (1985), pp. 612-618.
40. Ono, M., K. Yamakawa, H. Kobayashi, and I. Itoh, I., "2-Tert-Butyl-5-Chloro-6-Nitrobenzoxazole, a Practical Synthetic Intermediate for 4-(Aryloxy)-5-Nitro-2-Aminophenols," *Heterocycles*, Vol. 27, No. 4 (1988), pp. 881-884.
41. Werstiuk, N.H. and C. Ju, "Protium-Deuterium Exchange of Benzo-Substituted Heterocyclics in Neutral D₂O at Elevated Temperatures," *Canadian Journal of Chemistry*, Vol. 67 (1989), pp. 812-815.
42. Dey, J.K. and S.K. Dogra, "Absorption and Fluorescence Characteristics of Some 2-Alkyl and 2-Aryl-Benzoxazoles in Different Solvents and at Various Acid Concentrations," *Indian Journal of Chemistry, Section A: Inorganic, Bio-inorganic, Physical, Theoretical & Analytical Chemistry*, Vol. 29A (1990), pp. 1153-1164.
43. Döpp, H. and D. Döpp, "1,3-Benzoxazole," in *Methoden der Organischen Chemie (Houben-Weyl)*, Georg Thieme Verlag: Stuttgart (1993), pp. 1020-1194.
44. de Raadt, A., H. Griengl, M. Petsch, P. Plachota, N. Schoo, H. Weber, G. Braunegg, I. Kopper, M. Kreiner, and A. Zeiseret, "Microbial Hydroxylation of 2-Cycloalkylbenzoxazoles. Part III. Determination of Product Enantiomeric Excess and Cleavage of Benzoxazole," *Tetrahedron: Asymmetry*, Vol. 7, No. 2 (1996), pp. 491-496.
45. Kolenc, I., M. Kocevar, and S. Polanc, "Application of Oximes for the Transfer of a C-H Fragment," *Acta Chim. Slov*, Vol. 46, No. 2 (1999), pp. 281-288.
46. Clark, L.M., "The Quarternary Salts of Benzoxazoles," *Journal of the Chemical Society*, (1926), pp. 232-235.
47. Ott, D.G., F.N. Hayes, and V.N. Kerr, "Oxazole Quarternary Salts," *Journal of the American Chemical Society*, Vol. 78, No. 9 (1956), pp. 1941-1944.
48. Duclos, J.M. and P. Haake, "Ring Opening of Thiamine Analogs. The Role of Ring Opening in Physiological Function," *Biochemistry*, Vol. 13, No. 26 (1974), pp. 5358-5362.
49. Sainsbury, M., "Five-Membered Heterocyclic Compounds with Two Different Hetero-Atoms in the Ring," in *Rodd's Chemistry of Carbon Compounds*, Eds. S. Coffey and M.F. Ansell, Elsevier: New York (1986), p. 350.

